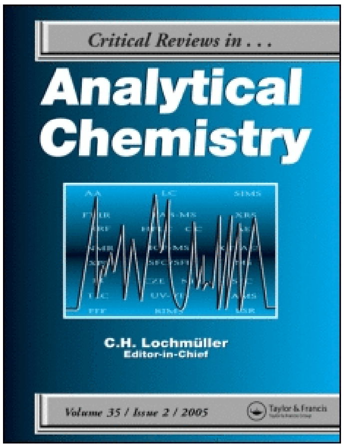

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ANALYSIS BY EMISSION, ABSORPTION, AND FLUORESCENCE OF SMALL MOLECULES IN THE VISIBLE AND ULTRAVIOLET RANGE IN GASEOUS PHASE

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I. INTRODUCTION

In past years, analytical atomic spectroscopy has been very successful in the field of quantitative analysis, particularly for the determination of traces in solid samples, solutions, and gases. These successes result from the excellent analytical characteristics of this technique:

1. *The detection ability,* which in most techniques is characterized by a high or even very high sensitivity and medium or good precision, permits determinations of major and minor constituents as well as traces and extreme traces.
2. *The accuracy* of the results is determined by the excellent apparatus and spectral selectivity, but negatively affected by numerous matrix interferences of physical and chemical origin.
3. There is a wide *applicability* of the technique, particularly for a large number of elements, the variability with respect to the kind and quantity of sample, and the possibility of making multielement analysis. Naturally these criteria differ with the individual methods. It may be added that the expenses, which consist of labor and apparatus cost, remain within reasonable limits.

Two major problems may, however, be deduced from the above. There are many matrix effects which may affect both the signals and the background. Table 1 presents a survey of the possible matrix interferences. Processes 1 and 2 are also known as chemical matrix interferences; process 3 is a physical matrix interference. Chemical matrix interference is more prevalent with low-temperature vapors between 1000 and 4000 K. With higher temperatures, the physical matrix effects are prevalent. Table 1 shows that formation or suppression of dissociation of thermally stable molecules and radicals may exert a significant effect on the accuracy of analytical atomic spectroscopy in emission as well as in absorption, not only in low-temperature vapors (flames, graphite tubes), but also in arcs and other spectroscopic sources.

With vapor temperatures of 1000 to 4000 K, mainly diatomic molecules and radicals exist primarily composed of one metal atom and one nonmetal atom. To a lesser extent triatomic and polyatomic molecules may also exist.

Another unsatisfactory aspect of analytical atomic spectroscopy results from the fact that many elements, but not all, may be easily determined, but in general nonmetallic elements are difficult to determine. This disadvantage arises for the following reasons: (1) the most sensitive resonance lines of the nonmetallic elements are partially situated in the vacuum ultraviolet, (2) these elements tend to form stable, hardly dissociable molecules, and (3) the substances are often easily vaporized but difficult to excite (Ta-

Table 1
MATRIX INTERFERENCES IN ANALYTICAL ATOMIC SPECTROSCOPY

Process	Influence on: Signal	Influence on: Background
Vaporization/condensation	Change of the free atom concentration of the analyte by incomplete or accelerated vaporization	Solid or liquid particles result in continuous spectra (AES) or continuous spectra and stray light (AAS)
Dissociation/molecule formation	And dissociation	Free molecules result in unresolved band spectra
Ionization/recombination	And by alteration of electron pressure	Continuous spectra from recombination

Table 2
RESONANCE LINES (nm), IONIZATION ENERGIES (eV), AND DISSOCIATION ENERGIES (eV) FOR SOME NONMETALS

B	249.7	C	165.6	N	120.0	O	130.0	F	95.5	nm
	8.3		11.3		14.4		13.6		17.4	eV
	2.8		6.2		9.8		5.1		1.4	eV
		Si	252	F	179	S	181	Cl	135	nm
			8.1		10.5		10.4		130	eV
					4.9		4.4		2.4	eV
				As	193	Se	196	Br	149	nm
					9.8		9.8		11.8	eV
					4.0		3.4		2.0	eV
						Te	214	I	178	nm
							9.0		10.4	eV
							2.7		—	eV

ble 2). Whereas analysis of nonmetallic substances has continuously been gaining in importance over the last three decades, the difficulties mentioned above have been encountered in analytical atomic spectroscopy. Alternative analytical techniques were also found to give unsatisfactory results. Thus, new spectroscopic variants were investigated, particularly those based on the fact that predominantly diatomic molecules, in addition to other molecular species, consisting of a metal and nonmetal are present in low-temperature vapors which can interact with electromagnetic radiation. The resulting band spectra may occur in emission as well as in absorption and fluorescence. After selection of appropriate operating conditions, they are used for the quantitative determination of the nonmetallic atoms. Molecular spectroscopy of low molecular weight molecules is closely related to common atomic spectroscopy.

In summary, it can be stated that while the band spectra of molecules and radicals produced in low-temperature vapors create interferences in analytical atomic spectroscopy, they also offer a chance for the analytical determination of nonmetals. Flames and electrothermally or flame-heated cuvettes are preferably used for the generation of vapors for such analysis, but in some cases other plasmas, e.g., arcs, inductively coupled plasma (ICP), and microwave-induced plasma (MIP), can be used. As most chemical matrix effects occur in vapors which have low temperatures, they may also be expected to occur with the techniques of molecular spectrometry. Since the problems and potentialities of emission and absorption techniques are somewhat different, there will be an appropriate structuring of the sections.

Table 3
DETECTION LIMITS OF SOME NONMETALS USING THE ICP

Element	Transition (nm)	Detection limit (μg/m*l*) Water	Organic medium
Sulfur	190.02	10	50
Phosphorus	214.91	0.03	0.05
Iodine	206.16	0.1	—
Carbon	193.09	1	—

II. PRESENT LEVEL OF NONMETAL ANALYSIS BY ATOMIC SPECTROSCOPY

A. Direct Analysis Procedures

In spite of the difficulties mentioned, atomic emission spectrometry (AES), atomic absorption spectrometry (AAS), and atomic fluorescence spectrometry (AFS) have been used for the direct determination of some nonmetals. Thus, for example, the copper-spark method,[1] the vacuum spark,[2] and recently, the ICP,[3-18] the MIP,[19-24] and the glow discharge[25] methods have all been used for the determination of halogens and other nonmetals. The application of ICP has, in several cases, offered quite good limits of detection (Table 3).

Direct techniques for Br-AAS[26] and S-AAS[27] have been developed using vacuum spectrometers. In some cases, AF measurements were used.[28,29] The problems with these techniques are (1) detection limits are only marginally good enough and (2) the methods are hardly applicable to routine analysis.

B. Indirect Analysis Procedures

Indirect procedures have been developed in AAS based on the principle that nonmetals and their counter ions form stable compounds with metals which are easily determined by AAS, thus permitting a more or less specific separation (precipitation, extraction, volatilization, etc.). A survey of those indirect AA techniques for F^-, Cl^-, Br^-, I^-, ClO_4^-, IO_3^-, PO_4^{3-}, SO_4^{2-}, SO_3^{2-}, and S^{2-} ions is provided in Reference 30. This paper contains another 48 original references.

Gutsche et al.[31] have recently described a method for the determination of fluoride by AAS after separation as SiF_4. The detection limit is 0.2 and 30 μg fluoride when a graphite tube or a flame, respectively, is used. Battistoni et al.[32] described a method for chloride determination after separation as $CrOCl_2$ by Cr-AAS. The Hg-AAS by McHugh and Turner[33] and Chuchalina et al.[34] was also used for chloride determination. Kataoka et al.[35] determined perchlorate ions in the same way. Traces of iodide were determined after reaction with Hg^{2+} by Hg-AAS.[36]

A great number of indirect AA determinations was developed for the determination of sulfur or sulfur-containing ions. Marshall and Midgley[38] determined SO_3^{2-} ions and SO_2 in picogram amounts by Hg-AAS. S^{2-} ions were determined[39] by Zn-AAS. In most cases, the Ba-AAS was used for the determination of SO_4^{2-} ions.[37,40-43] Sasaki and Nagumo[44] used solid $BaCrO_4$ which forms $BaSO_4$ with SO_4^{2-} ions. The free CrO_4^{2-} ions can be determined by Cr-AAS. Yoshida and Takahashi[37] reported on the determination of S^{2-} ions after formation of HgS and subsequent determination of excessive Hg^{2+} by a cold-vapor-AAS technique. The detection limit is 0.02 μg. Riddle and Turek[45] determined SiO_3^{2-} and PO_4^{3-} ions after formation and extraction of heteropolymolybdic acid, the Mo being measured by AAS. These indirect procedures are all based on the distribution of an added substance between two phases, one of which is measured by AAS.

Apart from these procedures, indirect techniques have also been developed for AAS which are based on the effects of the formation of molecules between the anion of interest and an easily determined cation. This principle has been predominantly applied to the determination of fluoride.

In the presence of F^- ions in the solution containing Mg^{2+}, the thermally stable MgF molecule is formed (among others) during vaporization. Depressions of the AA signal of Mg are proportional to the F^- concentration.[46,47] Determinations are possible in the range ca. 0.2 to 20 μg F^-/mℓ. In contrast to this, the AA signal of Zr is proportionately increased in the presence of F^-. Easily dissociable ZrOF molecules have been reported to have formed.[48] The determinations are possible in the range between 5 and 200 μg F^-/mℓ. An interesting variation of this was reported by Gutsche et al.,[49] who used a gas chromatograph coupled to a special furnace to produce a constant partial pressure of Na vapor. With the use of an argon gas stream, the Na vapor was guided through a heated graphite tube cuvette, wherein the Na-AA signal was measured. If the separated organic compounds are introduced into this gas stream, the NaF molecule is formed from this Na in the presence of organic compounds containing F. It is stable even in the graphite cuvette, so that a depression of the Na-AA signal is measured, it being proportional to the F^- concentration. They obtained an excellent detection limit of 0.8 ng F^-. Problems were encountered with routine analysis, however.

III. THEORETICAL ASPECTS OF THE SPECTROSCOPY OF DIATOMIC MOLECULES

A. Theory and Term Symbols

It is not the purpose of this paper to present a comprehensive treatise on the spectroscopy of diatomic molecules. Reference must be made therefore to appropriate monographs such as those by Gaydon[50] and Herzberg.[51] The following serves as an introduction to the basic principles and the symbols used.

The energy of a molecule can be expressed as the sum of the electronic energy (E_e), vibration energy (E_v), and rotation energy (E_r), according to

$$E = E_e + E_v + E_r \tag{1}$$

The rotation energy is given by

$$E_r = \frac{h^2}{8\pi^2 I} J(J + 1) \tag{2}$$

where J = rotation quantum number 0, 1, 2 . . . , I = moment of inertia μr^2 (r = internuclear distance, μ = reduced mass), and h = Planck's constant. For the value J = 0 there is one and for $J \neq 0$ several eigen-functions.

The vibration energy of a harmonic oscillator is given by

$$E_v = h\,\nu_{osc}\,(v + 1/2) \tag{3}$$

where ν_{osc} = vibration frequency and v = vibrational quantum number 0, 1, 2 . . . An anharmonic oscillator model is used to describe real molecules and correction terms are applied to the energy levels given in Equation 3.

The energy of the molecular electronic states depends on the quantum numbers n, l, and λ, n being the principle quantum number and l the subordinate quantum number. For a given l the quantum number λ is given by:

$$\lambda_i = m_l = l, l - 1, \ldots 0, -1 \ldots - l, \tag{4}$$

The quantum number λ corresponds to the magnetic quantum number in atoms. It results from precession of the orbital angular momentum about the direction of the nuclear magnetic field. The molecular orbitals associated with λ = 0, 1, 2, . . . are designated as molecular orbitals σ, π, δ in analogy with atomic orbitals. Orbitals with λ = 0 are not degenerate, and orbitals with λ ≠ 0 are doubly degenereate, i.e., the energy value of +λ condition corresponds to that of the −λ condition.

The orbitals are designated as follows: n, l, e.g., 1 s as the lowest orbital of the H_2^+ ion. The fourth quantum number s may, just as with the atom, take values $\pm 1/2$. With multielectron systems, the total electronic angular momentum of the molecule is given by the sum of the orbital angular momentum λ_i of all electrons, that is:

$$\Lambda = \Sigma \lambda_i \tag{5}$$

For the values Λ = 0, 1, 2, 3, . . . in analogy with the terminology used with atoms the symbols Σ, Π, Δ, Φ, etc. are applied.

To determine the total spin state of the molecule the individual spins of the electrons must be added vectorially:

$$S = \Sigma s_i \tag{6}$$

In the direction of Λ this quantity may assume all integral values between +S and −S.

From this, the multiplicity rule of 2 S + 1 results. This value is indicated at the top left-hand side of the λ symbol. In addition to these symbols, + or − is added to the top right-hand side of the Λ symbol, depending on whether the associated wave function is symmetrical or antisymmetrical with respect to inversion through the origin, chosen at the center of symmetry of the molecule. The values of Ω are added at the lower right-hand side of the Λ symbol, according to Ω = Λ + Σ. This is the quantum number for the resulting orbital angular momentum.

The spectroscopy to be considered here is concerned with changes in the electronic states, e.g., electronic spectra. These electronic spectra coincide with the energetically lower vibration and rotation spectra, i.e., in absorption or emission there are transitions from the rotation levels of various vibrational levels of one electronic state to the rotation levels of vibration level of another electronic state. It has become a tradition in molecular spectroscopy that when designating such a transition the symbol of the energetically higher state is always written first.

A few selection rules hold for the possible transitions, some of which are given below:

1. $\Delta n = \text{random}$
2. $\Delta\Lambda = 0, \pm 1$
3. $\Delta S = 0$
4. $+ \leftrightarrow -;\ + \not\longleftrightarrow +;\ - \not\longleftrightarrow -$
5. $\Sigma^+ \leftrightarrow \Sigma^-;\ \Sigma^+ \not\longleftrightarrow \Sigma^+;\ \Sigma^- \not\longleftrightarrow \Sigma^-$
6. $\Delta J = 0, \pm 1;\ J = 0 \not\leftrightarrow J = 0$
7. $\Delta v = \text{random}$

Electronic transitions which are connected with vibrational transitions are designated as $v'' - (v')$ progressions if the transitions occur from a vibrational level of an upper (lower) to a lower (upper) electronic state. To each band of an electronic transition a particular Δv value is assigned due to the change in the vibrational state. The fine structure of the band is determined by the overlapping of rotational states. The intensities of individual bands depend on the Δv values. These dependencies may be explained by the Franck-Condon principle (compare with Reference 51). Often the 0,0 transitions are the most intensive.

Apart from the more or less structured band spectra, continua also exist. With absorption processes, dissociation and ionization are possible sources for the production of continuous spectra. Dissociation continua, which are directly adjacent to the band spectra, occur very rarely however because transitions from the lower to upper electronic state would require large changes to occur in the internuclear distance. Ionization continua are even rarer.

Of greater importance are the processes of predissociation which are based on Auger processes. Auger processes involve widening of absorption lines, weakening of emission lines, and resonance phenomena, which eventually lead to diffuse spectra. Predissociation occurs in a molecule when absorption of radiation places it in a bound excited electronic state situated above the first dissociation limit where it is overlapped with a continuum of energy levels. The molecule may dissociate due to nonradiative transitions to a repulsive electronic state. With diatomic molecules, predissociations due to the electronic and rotational transitions play a particular role. These transitions are also governed by certain selection rules. The inverse process, designated as inverse predissociation, plays an appropriate role in molecular emission.

If the continuous energy level range lies above the ionization limit, nonradiative transitions from a monoenergetic level to the continuum may also bring about a type of ionization called preionization.

A very comprehensive survey of spectroscopic data on diatomic molecules is given in References 52 and 53. Data concerning the dissociation energies of molecules (E_D) are given in both monographs. As these data are not homogeneous, the following conversions are given:

$$
\begin{aligned}
1 \text{ eV} &= 3.8263 \times 10^{-20} \text{ cal} \\
&= 1.602 \times 10^{-19} \text{ J} \\
&= 8065.73 \text{ cm}^{-1} \\
&= 23.061 \text{ kcal/mol} \\
&= 96.552 \text{ kJ/mol}
\end{aligned}
$$

All energies are reported in eV throughout this paper.

The first prerequisite for the occurrence of spectra of diatomic molecules is the existence of the molecules. In principle, the concentration of diatomic molecules and radicals depends on their stability, i.e., on the magnitude of their dissociation energy, on the temperature of the vapor, and on the concentration of the molecule-forming atoms. The latter is of particular importance if the concentrations of both kinds of atoms are significantly different. As the vapor temperatures are generally not well known, calculations of molecular concentrations are also problematic, very time consuming, and of little use for practical analysis.

By considering only low-temperature vapors in the range 1000 and 4000 K, diatomic molecules may be qualitatively classified into several groups according to their dissociation energies: $E_D > 6$ eV = very stable molecules; E_D: 4 to 6 eV = stable molecules; E_D: 2 to 4 eV = molecules with little stability; $E_D < 2$ eV = unstable molecules. The first two groups are the most relevant to analysis; however, useful correlations between molecules of the two latter groups may also be utilized, whereas all interactions of free molecules or radicals with electromagnetic radiation are of analytical relevance. Transitions between discrete energy levels are particularly useful for analytical determinations as these bands are relatively narrow. All remaining phenomena have, since they appear as spectral background, a negative effect in atomic spectroscopy as well as in molecular spectroscopy, the two being closely related.

B. Using Diatomic Molecules for Determination of High Temperatures in Plasmas

A number of determination methods of plasma temperatures by spectroscopy of diatomic molecules have been described. In this paper we want only to make reference to this fact. A full discussion is impossible.

For temperature measuring, electron-excited spectra with their components of vibration and rotation can be used. In most cases, rotational lines are used. For example, Ochkin and Savinov[54] determined temperatures of a glow discharge by using rotational lines of the OH and CN radicals. We also used the CN radical for determination of arc temperatures.[55] Lavrov and Otorbaev[56] used the band spectra of D_2 and H_2 molecules for the determination of gas temperatures in low-pressure discharges. Similar theoretical studies of rotational spectra in emission mode are described by Delaval et al.[57] for the unstable FeCl molecule.

C. Studies of IR-Spectra of Some Molecules — Detection of New Molecules

In this section we will give only some remarks in relation to unstable molecules.

Schnöckel[58] described the possibility of formation of AlOX molecules by condensation of AlX (X = Cl, F) and O. By IR spectroscopic measurements it was possible to detect such molecules and to determine bond energies.

From the analytical point of view this is important, because AlF and AlCl molecules are used for quantitative X^- determinations. The described reaction can be understood as a matrix interference. Similar types of reactions were observed between GaX and O[59] and AlX and HCl.[60] Also, for other metal halides such effects were studied, e.g., Zn, Cd, Hg, X = Cl, Br, I (compare with Reference 61).

D. Detection of Some Unstable Molecules in the Gas Phase

In the past, some studies were done by mass spectrometry to detect unstable molecules. In relation to our own investigation in the field of semiconductor materials,[62] we will show some examples.

Evidence was given by Grade et al.[62] for the existence of the gaseous ZnO molecule. A mean value of $E_D = 67.0$ kcal was obtained as dissociation energy. This first study was widened to such molecules as ZnS, ZnTe, CdTe, HgSe,[63] and CdO.[64] Recently, this high-temperature mass spectrometry was used for calculation of equilibrium constants for the vaporization and bond energies for MX molecules (M = Zn, Cd, Hg; X = O, S, Se, Te).[65,66] For our analytical purposes these papers show that many substances exist in the gaseous phase at sufficient concentrations.

IV. MOLECULAR EMISSION SPECTROSCOPY (MES) OF DIATOMIC MOLECULES

A. General Aspects

As described in Section III, high molecule concentrations are associated with low-temperature vapors. It is therefore not surprising that the first investigations on the analytical application of the spectra of diatomic molecules were made in flames. Following the trend to microanalysis, the molecular emission cavity analysis (MECA) technique was later developed which also relied on flames for excitation. To a lesser extent, electrically heated graphite tube cuvettes and other plasma-like arc discharges, etc. were also used (compare with References 67 and 68). The structuring of this section is in correspondence with the above statements.

Let us begin with the two basic principles of these techniques:

1. A solution in which a nonmetal (anion) must be determined is mixed with a second solution containing the metallic cationic component. The concentration of this additional component must be kept constant in all cases. The mixture is introduced into the vapor where molecule formation takes place.
2. A gas stream containing the nonmetallic component in a bound or elementary state is brought into contact with the surface of metallic component (e.g., at the exit of a gas chromatograph). A reaction will take place there in the course of which the appropriate diatomic molecule or radical is formed. The gas stream is then introduced into the plasma.

B. Analytical Applications of MES Using Flames

1. Introduction

The first observation of CuX bands (X = halogen) was published as early as 1845.[69] Several spectroscopic studies without analytical application followed.[70-72] These observations found an early analytical application to the qualitative detection of halogen-containing organic compounds in the well-known Beilstein test.[73] Here the second principle according to Section IV. A is realized. Halogens or pseudohalogens,[74] which originate from the combustion of appropriate organic compounds, react with a hot Cu surface. In this simplest procedure a Cu wire is brought directly into contact with the flame, thus forming CuX molecules. These CuX molecules react with the flame gases and form CuO and CuOH molecules resulting in the well-known green color of the flame. The Beilstein test was later improved with respect to apparatus[75] and appropriate devices were patented[76,77] (e.g., the van der Smissen burner).[77] An application of it to gas chromatography (GC) was also described.[78] Also, as early as the past century the Salet effect was described,[79,80] which was explained as an emission by the S_2 and the HPO molecule.

2. Excitation Mechanisms of ME of Diatomic Molecules

The excitation of molecular species to MES is produced by absorption of thermal or chemical energy. The prerequisite for a merely thermal excitation is the existence of thermal equilibration. The distribution among the various discrete energy levels of rotation, vibration, and electronic excitation may be calculated from the Boltzmann distribution law from which a direct relationship between concentration and emission intensity may be derived.

In those cases where deviations from thermal equilibrium occur, there may be an "overexcitation". Such deviations are generally found in flames containing excess concentrations of free radicals arising from combustion processes. The recombination of such radicals liberates free chemical energy, which with an appropriate transfer of energy may lead to the emission of typical molecular bands. This process is called chemiluminescence. There may be genuine chemiluminescence when the emitting particles are directly formed by chemical reactions or induced chemiluminescence, which occurs when the chemical energy liberated in one recombination reaction is transferred to a third particle, which then is emitted. Genuine chemiluminescence may occur by various mechanisms. Additionally, inverse predissociation must also be mentioned. Examples of induced chemiluminescence are the transfer of recombination energy from $H^\cdot$ radicals or $H^\cdot$ and $OH^\cdot$ radicals. The light intensities originating from chemiluminescence depend not only on the concentration of the emitting species, but also on the flame and plasma concentration. It may be stated that the major portion of intense band emission in low- and medium-temperature flames is based on chemiluminescence. For theoretical details we refer the reader to original papers and summarizing monographs.[51,81-92]

We will mention that chemiluminescence does not exist only for diatomic molecules. Reaction of alkali metals with halogenated compounds very often results in chemiluminescence.[93-95]

3. *Quantitative Determinations of Nonmetals by MES in Flames*

Preliminary investigations concerning the quantitative determination of chloride in sea water were carried out using CuCl-ME at 435 nm. A H_2-O_2 flame was used. Using 0.31 M $Cu(NO_3)_2$, linear intensity-concentration relations were obtained for a concentration range of 40 to 5000 μg Cl^-/m*l*.[96] The presence of Br^- and I^- ions had a negative effect due to spectral overlap. Tests were also made for the quantitative determination of organic Cl compounds (herbicides, chloroform, and others).[97,98] The detection limits amounted to 175 μg Cl/m*l*, which was not quite as good as above. In this case, the substances were dissolved in the polar organic solvent dimethylformamide and introduced into a H_2-O_2 flame as an aerosol. The DMP contained the Cu^{2+} ions as well. The first application of the SrF-ME in a H_2-O_2 flame was carried out on the determination of freon 12 in air; 47 μg F/*l* air could be detected.[99] These preliminary studies were completed by Gilbert,[100] who modified the van der Smissen burner.[77] The reason for his study was the nonspecificity of the CuH-, CuO-, and CuOH-ME for the detection of halogens. Copper was replaced by an indium-coated tube and the emission intensity of the InCl molecules formed at 359.9 nm[100,101] in a cool H_2 air flame was measured.

About this same time there were attempts to utilize the Salet effect[79,80] for the specific detection of S-containing organic compounds by S_2 emission[102,103] and for P-containing compounds by HPO-ME,[103-106] following their separation by GC. Spectroscopic investigations in H_2-fuel-rich flames were carried out by Syty and Dean.[107]

Attempts were also made to utilize the emission of the PO radical for the determination of PO_4^{3-}. Davis et al.[108] used a H_2-O_2 flame. Measurement at 540 nm made it possible to detect 8 μg P/m*l*. Skogerboe worked with a H_2 air flame and determined 5 μg PO_4^{3-}/m*l* by measurement of the PO-ME at 246.4 nm.[109] Daidoji et al.[110] also measured the PO-ME and PO-MA in some flames. Primarily two research teams subsequently dealt with the analytical application of MES of diatomic molecules: Dagnall, Thompson, and West (U.K.), and Gutsche, Herrmann, and Rüdiger (F.R.G.). Recently a third team took up studies: Henrion and Marquardt (G.D.R.).[67,68]

Progress in the study of the less stable molecules was achieved after introduction of the relatively cool H_2-N_2 diffusion flame.[111] With this flame Dagnall et al.[111] succeeded in utilizing emissions from the S_2 molecule at 384 nm for the determination of S-containing substances in the concentration range 6.4 to 500 ppm S. Similarly the emission of the triatomic HPO molecule was used at 528 nm for the determination of PO_4^{3-} down to traces of 0.1 ppm P.[112] An improvement in this detection limit to 0.007 μg P/m*l* by measurement of the HPO-ME occurred later.[113] These studies were also used for the quantitative determination of SO_4^{2-} and PO_4^{3-} in aqueous systems. Detection limits of 0.1 μg S/m*l*, 1.3 μg P/m*l*,[119] and 1.2 μg P/m*l*[115] were obtained. P-compounds were also detected in lubricants by HPO-ME in H_2-N_2 diffusion flames in the concentration range 0.009 to 0.2% P.[116] Combination of these flame techniques with the carbon filament atomizer (CFAR) provides very good absolute detection limits with 1-μ*l* samples. S_2-ME succeeded in detection of 0.5 ng S, HPO-ME 4 ng P.[117] Recently, calculations of concentrations of S_2 molecules were carried out in flames by MES.[118] The optimum temperature range was found to be in the order of 2200 K.

The emission of the SnH molecule in diffusion flames was also studied.[119] The main purpose was not the determination of a nonmetal but spectroscopic studies of this molecule in general. Tin concentrations were detected down to 1.5 μg/m*l*.

Equally cool flames were used for studying the spectra of the InCl, InBr, InI, GaCl, GaBr, and GaI molecules. Appropriate band maxima were found at 360, 376, 410, 338.4/334.7, 354.9/350.3, and 391.1/386.3 nm, respectively. The possibility of detecting halides with this molecule was discussed.[120]

Similarly, spectroscopic studies in the region 700 and 280 nm, which were carried out using a capillary burner with a H_2-N_2 diffusion flame, did not serve for direct determination of specific species but for the detection of volatile fluorides.[121] Using solutions of As, B, C, Ge, I, Mo, P, Re, Sb, Se, Si, Te, and W in a mixture with fluoride, a number of bands were found, all of which, however, could not be identified. When occasion arose, these results could be used for clarification of unspecific background emission or other interferences.

Analytical aspects were emphasized much more by the second research team. With the use of a special H_2 air burner, the studies initiated by Gilbert[100] for determination of Cl by InCl-ME at 359.9 nm were continued. The technique is based on the burning of H_2 in a closed space in a deficiency of air. The vaporized sample is introduced into this gas mixture. The hot mixture is guided along a Be bronze ring coated with indium which is heated to 473 K. InCl molecules are formed by reaction between the Cl-containing organic compounds and the indium and emit the typical InCl bands in the course of subsequent combustion in air. At the time of the first publication,[122] the intensity was measured using a spectrophotometer. In the course of the determination of the insecticide lindane, 0.16 μg Cl was detected. Similar results were obtained using a considerably cheaper filter photometer which was provided with a metal interference filter having a maximum transmission of 359 nm and a half width of 7 nm.[123] When this detector system was combined with a gas chromatograph, the detection limit could be lowered to 0.003 μg Cl.[124,125] A comparison is also reported in Reference 126. Another study of InCl-ME was made by Chen[127] in his dissertation work.

These studies were also applied to the determination of Br by InBr-ME at 372.7 nm.[128] Likewise, a gas chromatograph with the described H_2 air burner was used. This apparatus was capable of detecting 0.7 ng Br bound to organic compounds. Practical use of the technique was made in CH_3Br residue analysis in cocoa,[129] and in the determination of Br^- ions and Br-containing compounds in urine.[130]

Organically bound Br was determined by other authors by CuBr band emission at 434.1 nm.[131] In order to obtain a stable and intense CuBr spectrum, combustion gases were maintained at high oxygen pressure and low hydrogen flow rate. *p*-Dibrombenzene was used as the standard bromine compound and Cu-containing dimethyl formamide as solvent. The determinable concentration range of bromine is 0.025 to 0.2 mol/*l*.

In a subsequent paper, these principles were applied to the determination of I-containing compounds after their separation by GC. InI-ME was measured at 409.9 nm. The detection range of the technique lies between 0.01 and 1.4 μg I.[132] The temperature of the indium-coated Be bronze ring had to be increased to 573 K because of the higher melting point of InX (F_p: 624 K). The technique was also applied to the simultaneous determination of Br- and I-containing drugs.[133]

A fluoride-specific detector for GC is described in Reference 134. The basic principle is the supply of an argon stream to a microburner which operates on C_2H_2-O_2. Ca-vapor, heated in a furnace, is added to the argon stream. Simultaneously, the F-containing organic compounds coming from the gas chromatograph are introduced into the flame where the CaF molecule is formed from the Ca and the F released by decomposition of the organic compounds. The emission from the CaF molecule is measured at 529.9 nm.

With this apparatus about 50 ng F may be detected. In order to improve the F detection limit, further MF-ME bands (M in MF: Ba, Sr, Ca, Mg, Cu) were studied and tested for their analytical applicability. The MF bands for M = B, Be, Bi, I, La, Mn, Pb, S, Sb, Si, and Te could not be detected. Optimum signal-background ratio was obtained with the SrF-ME band at 585 nm, which, however, suffered from severe interference by Na atomic emission at 589 nm, so that for the further work the CaF-ME was recommended.[135] A simplification of the technique[134] is possible when a filter photometer provided with a metal interference filter (D_{max}: 529.5 nm) is used. An improvement of the detection limit by a factor of 1.5 was achieved.[136] For determination of F^- in aqueous media, the SrF-ME at 580 nm is suitable when a H_2-O_2 flame is used. The sample containing the F^- and the added Sr^{2+} is introduced into the flame as an aerosol using an atomizer. With a sample volume of 0.2 mℓ, 9.2 μg F^- may be detected.[137] An improvement in the detection limit over that described in Reference 136 is possible when CaF-ME is used.[138] In this manner, the detection limit is increased to 11 ng F.

Recently, a combination of the halogen-specific indium burner and a high-pressure liquid chromatograph was described.[139,140] A spectroscopic F detector for the HPLC was also developed using a H_2-O_2 flame for excitation of the CaF-ME.[141]

With use of a laminar flow H_2-N_2 diffusion flame, the third research team succeeded in obtaining InF-ME at 328.2 and 319.7 nm.[142] Extensive studies on the ME of InX and GaX species (X = Cl, Br, I) were carried out in the same laminar flame. It was observed that the 0.0 transitions of the A and B band system were most intense.[143] Emission from TlX molecules (X = Cl, Br) was also detected.[144]

Studies on the CH- and the C_2-ME of halogenated hydrocarbon compounds contributed to the elucidation of excitation mechanisms.[145] Energetic and spectroscopic observations lead to the conclusion that the $H^{\cdot}$ radical recombination (E = 4.48 eV) and the recombination of $OH^{\cdot}$ and $H^{\cdot}$ radicals (E = 5.12 eV) represent energy-releasing processes. Thus in relatively cool flames, InCl-ME could be observed at 267.2 and 267.9 nm and GaCl-ME at 249.1 nm (this corresponds to 4.99 eV.[146] Summaries of these studies are contained in References 92, 147, and 148.

There are some new studies[149] about excitation mechanisms. From the behavior of the intensities of excited and nonexcited MX species and the existence of InF bands in the C branch with the high excitation energy of 5.3 eV in the H_2-N_2 diffusion flame, it could be derived that the excited state results from the reaction of metal and halogen atoms. Furthermore, the experimental results of MX intensity measurements indicate reactions of excited molecules with particles of flame gases. In the mentioned publication,[149] a survey of the analytical possibilities of MX-ME is given (when M is Cu, Ga, In, Tl, and X is F, Cl, Br, I) (compare with Table 4). Also, this organically bound halogen was determined. Additional information about molecular emission of alkaline earth — halogen molecules — was given in Reference 150.

Recently, several other studies were published in this field. Butcher and Kirkbright[151] determined the NH_4^+ content of a sample after removal of NH_3 by alkali and introduction of the ammonia into a H_2-N_2 diffusion flame. NH-ME was measured at 336 nm; 1 μg NH_3 could be detected. Determination of the S content in steel was obtained in a similar manner using S_2-ME.[152] A technique utilizing CN-ME at 388.2 nm as an internal standard to improve the reproducibility of the determination of Ba and Al by atomic emission in C_2H_2-N_2O flames is described by Verbeek and Ure.[153]

Interesting information was recently given concerning the determination of As and Sb by AsO- and SbO-ME at 429 and 369 nm, respectively.[154] After production of AsH_3 and SbH_3 by a reducing agent, those hydrides were introduced into a H_2-N_2 diffusion flame which was surrounded by oxygen. Due to the decomposition of the hydrides, the free atoms of As and Sb (possibly also their molecules such as As_2) were formed and interacted with O according to: $As + O \rightleftharpoons AsO$ and $Sb + O \rightleftharpoons SbO$, respectively. Due to genuine chemiluminescence, these molecules radiate energy at the wavelengths mentioned. Detection limits of 50 ng As and 100 ng Sb were reported.

The application of the CaOH-ME at 554 nm for determination of Ca by flame spectrophotometry has been well known for a number of years. Recently, a paper was published in which the matrix interferences were studied.[155] The same authors described cationic interferences in the molecular emission of the SrOH molecule at 606 and 671 nm. By combined use of B and La compounds, the Al interference overcomes.[160] Similar statements were given by De la Guardia Cirugeda et al.[157,158]

Long and Boss[159] and Wood et al.[160] explained the signal depression of Ca, Sr, and Ba atomic and CaOH, SrOH, and BaOH molecular emission by phosphorus with molecule formation (e.g., $CaPO_x$). In order to elucidate background interferences, the flame emissions of several MCl_x (M = Fe, Si, Ti, Al) molecules in H_2-O_2-N_2 flames were studied.[161]

ME of the triatomic molecule BO_2 has also been used for analysis. A common Bunsen flame is used for boron determination through $B(OCH_3)_3$, which is obtained from the borates or boric acid by reaction with CH_3OH and conc. H_2SO_4.[162-165] In this manner, 5 μg B may be detected. Borate ions were transferred into BF_4^- by F^- addition. The BF_4^- may be extracted with tetrabutylammonium into MIBK and the extract directly introduced into a H_2-O_2 flame.[166] Studies on the influence of the state of binding were carried out.[167] Recently, Siemer[168] described a very sensitive determination of B by BO_2-ME.

When a H_2-O_2 flame free of C is used, carbon compounds may be detected by CH-ME at 431.5 nm and by C_2-ME at 516.5 nm. The detection limits lie in the μmol range.[169]

Recently, S_2-ME was applied as a field method for determination of S in petroleum products[170] and of SO_2 in aqueous systems. In aqueous systems, the SO_2 is removed by acids, whereas the petroleum must be burned in order to produce SO_2. The SO_2 which has been obtained from an aqueous solution is absorbed, for enrichment, in Na_2HgCl_4 solutions and then removed again by acids. With these techniques it is possible to detect 6 ng S. Equilibrium concentration of AlCl, AlH, and AlO molecules in C_2H_2 air flames and C_2H_2-N_2O flames was determined by Wittenburg et al.[171] by measurement of ME.

Table 4 gives a survey of the analytical application of ME in flames. It may be seen that the relevant analytical results were obtained by combining these methods with GC. The detection ranges obtained permit operation in the field of trace analysis. When GC is applied, it must be noted that the organic molecules to which the halogens are bound exert strong matrix effects which influence the accuracy of the results. Therefore, in most cases, specific calibrations must be carried out for quantitative analysis. The analytical determination of substances in aqueous media must be optimized as a number of matrix effects affect the results here, too. The application of cool diffusion flames has been of particular significance for ME since they produce little background and high concentration of molecular species because of their low temperature.

C. Analytical Applications of MES Using MECA Technique

1. Introduction

The molecular emission cavity analysis (MECA) technique was developed by Belcher, Bogdanski, and Townshend. The first variant of the MECA technique, which was published 1973,[172] was based on the following principle: a few microliters of a liquid or several milligrams of a solid are placed in a cavity, and the substance evaporates as the cavity is heated. Molecules present in the cavity are excited to emission. Because the emission of some species is strongly influenced by the surrounding atmosphere (H_2, O_2, halogens, etc.), some variants of cavities were constructed (e.g., the oxy cavity). The most number of papers dealing with MECA technique belongs to this

Table 4
ANALYTICAL APPLICATIONS OF MOLECULAR EMISSION IN FLAMES

Molecule	Dissociation energy (eV)	Band (max.) nm	Type of flame	Substance determined: ion/atom/ compound	Detection limit	Combination with other methods	Ref.
CuF	4.4	493.2	C_2H_2-O_2	F^-	—	—	135
	4.4	569.4	H_2-N_2-dif.	F^-	10 mg/mℓ	—	149
CuCl	3.6	435	H_2-O_2	Cl^-, Cl-R	40 μg/mℓ	—	96—98
		526.2	H_2-N_2-dif.	Cl-R	1.1 μg/mℓ	—	149
		435.4	H_2-N_2-dif.	Cl^-	7 μg/mℓ	—	149
CuBr	3.4	487.9	H_2-N_2-dif.	Br^-	3 μg/mℓ	—	149
		434.1	H_2-O_2	Br-R	0.025 *M*/mℓ	—	149
CuI	2.0	507.3	H_2-N_2-dif.	I^-, R-I	0.3 *M*/ℓ	—	149
InCl	4.4	359.9	H_2-air	Cl^-	90 ng	—	100, 101
			H_2-N_2-dif.	Cl^-	—	—	120, 143
			H_2-air	Cl^-, Cl-R	160 ng	—	122, 123
			H_2-air	Cl-R	160 ng	GC	124—126
			H_2-air	Cl-R	—	HPLC	139
			H_2-N_2-dif.	Cl^-	4 μg/mℓ	—	149
			H_2-N_2-dif.	Cl-R	0.28 *M*/ℓ	—	149
InBr	4.0	376	H_2-N_2-dif.	Br^-	—	—	120, 143
			H_2-N_2-dif.	Br^-	4 μg/mℓ	—	149
			H_2-N_2-dif.	Br-R	0.48 *M*/ℓ	—	149
		372.7	H_2-N_2-dif.	Br-R	0.7 ng	GC	125, 126
			H_2-air	Br-R	—	GC	129
			H_2-air	Br^-, Br-R	6 ng/mℓ	—	130
			H_2-air	Br-R	—	HPLC	139
InI	3.4	409.9	H_2-N_2-dif.	I-R	—	GC	120, 125, 143
InI	3.4	409.9	H_2-air	I^-	100—1400 ng	GC	132, 133
			H_2-air	I-R	—	HPLC	139
			H_2-N_2-dif.	I-R	—	—	149
InF	5.4	328.2	H_2-N_2-dif.	F^-	—	—	142
			H_2-N_2-dif.	F^-	0.7 μg/mℓ	—	149
GaF	6.0	299	H_2-N_2-dif.	F^-	10 mg/mℓ	—	149

Table 4 (continued)
ANALYTICAL APPLICATIONS OF MOLECULAR EMISSION IN FLAMES

Molecule	Dissociation energy (eV)	Band (max.) nm	Type of flame	Substance determined: ion/atom/ compound	Detection limit	Combination with other methods	Ref.
GaCl	4.9	338.4/334.7	H_2-N_2-dif.	Cl^-	—	—	120, 143
		338.44	H_2-N_2-dif.	Cl^-	350 µg/mℓ	—	149
GaBr	4.3	354.9/350.3	H_2-N_2-dif.	Br^-	—	—	120, 143
			H_2-N_2-dif.	Br^-	250 µg/mℓ	—	149
GaI	3.5	391.1/386.3	H_2-N_2-dif.	I^-	—	—	120, 143
			H_2-N_2-dif.	I^-	130 µg/mℓ	—	149
TlCl	3.8	322.1	H_2-N_2-dif.	Cl^-	3.5 mg/mℓ	—	149
TlBr	3.4	343	H_2-N_2-dif.	Br^-	4 mg/mℓ	—	149
CaF	5.5	529.9	C_2H_2-O_2	F^-,F-R	10—50 ng	GC	134, 136, 138
SrF	5.6	580	H_2-O_2	F-R	50 ng	—	99
			C_2H_2-O_2	F^-	—	—	135
			H_2-O_2	F^-	9.2 µg/mℓ	—	137
		578	H_2-air	F^-	45 µg	—	149, 150
SrCl	4.2	636	H_2-air	Cl^-	220 ng	—	149, 150
BaF	6.05	495	C_2H_2-O_2	F^-	—	—	135
BaBr		536	H_2-air	Br^-	3.3 mg	—	149, 150
BaI		561	H_2-air	I^-	7.8 mg	—	149, 150
MgF	4.8	359.4	C_2H_2-O_2	F^-	—	—	135
S_2	4.4	384	H_2-N_2-dif.	S	6.4 µg/mℓ	—	111
			H_2-N_2/CFAR	SO_4^{2-}	0.1 ng	—	132
			H_2-air	S-R	0.2 ng	GC	102, 103, 107
PO	5.4	540	H_2-O_2	PO_4^{3-}	8 µg/mℓ	—	108
		246.4	H_2-air	PO_4^{3-}	5 µg/mℓ	—	109
HPO	—	528	H_2-N_2-dif.	P	0.1 µg/mℓ	—	107, 112
			H_2-N_2/CFAR	PO_4^{3-}	4 ng	—	132
			H_2-N_2-dif.	PO_4^{3-}, P-R	0.009%	—	116, 117
			H_2-air	P-R	0.2 ng	GC	103—106
		520	H_2-N_2-dif.	PO_4^{3-}	7 ng/mℓ	—	113
		526.2	H_2-air	PO_4^{3-}	1.2 µg/mℓ	—	115

2.7	609.5	H_2-N_2-dif.	Sn	1.5 μg/mℓ	—	119
3.2	336	H_2-N_2-dif.	NH_4^+	1 μg	—	151
6.1	429	H_2-N_2-dif./O_2	As	50 ng	—	154
4.0	369	H_2-N_2-dif./O_2	Sb	100 ng	—	154
—	518	CH_4-air	BO_3^{3-}	5 μg	—	162—164
		C_2H_2-O_2	BO_3^{3-}	50 μg/mℓ	—	165
		H_2-O_2	BO_3^{3-}	—	—	164
	548	H_2-air	BO_3^{3-}	0.2 μg	—	168
3.4	431.5	H_2-O_2	C-compound	μmol	—	167
6.2	516.5	H_2-O_2	C-compound	μmol	—	167

conventional MECA. In addition to this direct analysis of microsamples, it is possible to use MECA technique as a detector for vaporization techniques (MECA-VAP) or chromatographic methods (MECA-GC, MECA-HPLC). Excitation is mainly produced by chemical energy (as described in Section IV.B.2), i.e., in many cases chemiluminescence is involved. Within the last decade, the MECA technique has been applied to the study and analysis of several systems. These are summarized in a number of surveys[173-184] as well as a monograph.[185] In the following section we will give a short survey about the analytical results of the MECA technique.

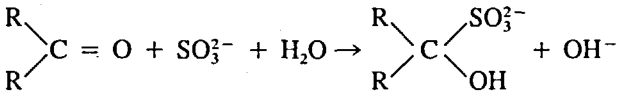
2. Quantitative Determinations by the MECA Technique

a. Sulfur, Selenium, Tellurium, and Compounds Which Contain These Elements

In the first paper on the MECA technique mentioned above,[172] S_2-ME at 384 nm was applied to the determination of SO_4^{2-} and sulfur-organic species. Quantities as small as 10 ng S were detected. These studies were continued in a second paper dealing with the determination of Se and Te.[186] Observed emissions were assigned to the Se_2 and SeO and the Te_2 and TeO molecules, respectively. Optimum Se_2-ME is obtained at 411 nm. The technique was applied to the determination of Se in H_2SO_4 and in Se-organic compounds. The Se-organic compounds are first oxidized in O_2. Between 0.4 and 4 μg Se may be detected. Optimum Te-ME is observed at 500 nm. Determinations are possible in the microgram range (compare with Reference 187). As for the determination of the elements of the sixth main group of the periodic table, studies were continued mainly for sulfur. Presumably the possibility of determining Se and Te is better by other techniques, e.g., AAS. The fifth paper on the MECA technique[188] reports determination of the following S-containing anions: SO_3^{2-}, SO_4^{2-}, $S_2O_8^{2-}$, S^{2-}, SCN^-, and $S_2O_3^{2-}$. Depending on the type of substance, decomposition in the cavity may occur at different times, i.e., at different temperatures. Consequently, S_2-ME occurs at different times, thus offering the possibility of developing techniques for the simultaneous determination of binary mixtures such as SO_3^{2-}/SO_4^{2-} and $S_2O_3^{2-}/SO_4^{2-}$ (sixth paper[189]), as well as mixtures of the type $SCN^-/S_2O_3^{2-}/SO_3^{2-}/S_2^{2-}$ (ninth paper).[190] In all cases, S_2-ME at 384 nm was used for measurement. Application of special chemical treatment of the samples, e.g., phosphoric acid for improvement of fractionation, and use of Cu cavities improved the selectivity of the determination. Techniques were developed for the determination of SO_4^{2-} ions in urine in the concentration range 10 to 200 μg SO_4^{2-}/m*l*.[191] In some cases evaporation was promoted by addition of H_3PO_4.[188,190,191]

By addition of phosphoric acid, the matrix interference by forming of refractory metal sulfate is avoided. In order to decrease the effect of the build up of refractory compounds on the inner surface of the cavity, a silica cup was positioned within the cavity, which may be washed. By this technique, the determination of soluble sulfate in water or vinegar and in aqueous extracts of soils, dusts, and charcoal is possible. The accuracy of the results was proved by gravimetric and nephelometric measurements.[192] In a further publication, the influence of the concentration of phosphoric acid on the determination of the sulfate was investigated. It was found that concentrations of 10^{-3} *M* phosphoric acid depress the S_2-emission intensity, but concentrations of up to 0.1 *M* are necessary to eliminate cationic interferences.[193] Nevertheless, of the depressive influence, the addition of phosphoric acid is useful for complex systems.

Similarly, the determination of aldehydes and ketones with the MECA technique is based on the S_2-ME (11th paper).[194] Carbonyl compounds react with SO_3^{2-} as follows:



$$R_2C{=}O + SO_3^{2-} + H_2O \rightarrow R_2C(SO_3^{2-})(OH) + OH^- \qquad (7)$$

If appropriate mixtures are introduced into a stainless steel cavity, the S_2-ME peak produced by the SO_3^{2-} ion is produced first. About 10 to 20 sec later the S_2-ME peak arising from the organically bound sulfur is produced. The following determinations are possible: CH_2O, 2 to 750 μg; CH_3CHO, 0.05 to 1 mg; $(CH_3)_2CO$, 0.4 to 3.5 mg.

Schubert et al.[195] report on the simultaneous determination of SO_3^{2-} and SO_4^{2-} by MECA techniques. Interferences in the determination of sulfur and the application of these techniques to its determination in coal, polyurethane foam, and orchand leaves has also been reported.[196]

The determination of saccharin in soft drinks by its S_2 emission is also possible.[197] Because direct S_2 emission of such drinks was not observed, the saccharin was extracted by ethylacetate; 5 μl of the extract can be injected into the cavity, and the S_2 emission of these microsamples allows the saccharin determination in a level between 20 and 200 ppm.

The determination of sulfite in soft drinks is possible by injection of a 10-μl sample into concentrated phosphoric acid at a higher temperature.[198] The evolved SO_2 is determined by S_2-emission measurements. This is a procedure of MECA-VAP.

Also, trace concentration of sulfate can be determined by using a vaporization system.[199] The sulfate solution was injected into partially dehydrated phosphoric acid with tin as the reducing agent. The evolved gases were introduced into MECA cavity (compare also References 206 and 207).

An improved procedure for the determination of sulfite by MECA-VAP was described in Reference 200. Sulfite is converted to sulfur dioxide, which is introduced into the MECA cavity. The determination of 5 ng sulfur by S_2 emission is possible. The determination of some organic compounds is described in References 201 and 202.

In the 12th paper[201] on the MECA technique, detailed statements are made on the selective determination of organic S, P, Si, As, N, and C compounds in combination with their separation by GC. In reducing systems free from O_2, S_2, and HPO molecules emitted, after addition of small quantities of O_2, detection of AsO-, SbO-, SiO-, BO_2- and also of CH-, C_2-, and NH_3-ME is possible. With the use of indium, all halides may also be detected.

It is stated that the sensitivity achieved does not yet match that obtained by flame spectrophotometry. At best, 10 pg S_2, introduced for example as CS_2, are detectable. The relative wide applicability is the great advantage of the MECA technique over common flame spectrophotometry since it is possible to determine a number of additional elements by O_2 addition. Other compounds such as methylthionine are determined with the new MECA photometer MEP 101.[202]

Schubert et al.[203] continued their work about simultaneous determination of sulfide, elemental sulfur, sulfite, and sulfate by time-resolved MECA. A quartz-lined stainless steel cavity was used. A sample size of 1.5 mg gives detection limits in the picogram to nanogram range.

A determination of sulfur in selenium was described by Kouimtzis.[204] Microsamples of about 1 mg were combusted in a flask. The evolved SO_2 was adsorbed on 30 mg silica gel, which was inserted directly into the cavity. The detection limit lies at 40 ppm.

Cheng and Fernando[205] determined sulfur in sulfur-containing species in solids. They found that the argon-cooled hydrogen flame is better for the determination of sulfate alone and of sulfate in mixture with S_8, SO_3^{2-}, and S^{2-}. For the determination of elemental sulfur and SO_3^{2-}, the nitrogen-cooled flame is more useful. The detection limit lies in the parts per million range.

After the first above-mentioned determinations of Se compounds by Se_2 emission, this work was continued by combination of the hydride generation technique using $NaBH_4$ and MECA.[208] This is also a form of MECA-VAP.

A new method (see below)[209] was used for Se determination, but the sensitivity was poor. The principle of this new technique consists of using a flame generated within the cavity. In a more recent paper, the direct determination of SeO_3^{2-}, SeO_4^{2-}, or TeO_4^{2-} by Se_2 and Te_2 emission is described.[210] A carbon cavity was used. The sensitivity was enhanced by addition of citric acid, ascorbic acid, and glucose. Phosphoric acid also markedly enhanced the emission of the Se_2 from SeO_2. Depressive cationic effects on Se anions are avoided. In the case of Te, the addition of phosphoric acid was not useful because the green HPO emission bands at 526 nm overlap with the Te_2 bands at 500 nm.

Later, Se was determined in water after coprecipitation with hydrated Fe(III) oxide at pH 7 to 8. After precipitation separation and solving of the precipitate, the Se compounds were reduced to elemental Se by hydrazin or SO_2.[211] The Se was adsorbed on glass fiber filters which were inserted into the cavity. Se_2-ME was measured.

b. Halogens and Halogen-Containing Compounds

Several studies were carried out to enable the determination of halogens by MX-ME using the MECA technique. The first step studied the application of the Beilstein test (compare with Reference 173). Emissions are described which are based on the formation of CuCl, CuBr, and CuI molecules. Different from the Beilstein test, where the emissions are nonspecific for the various halogens (CuO-ME), the A bands of the CuCl, CuBr, and CuI molecules at 526, 488, and 509 to 511 nm, respectively, are utilized in these studies for determination of the X^- concentrations. Improved results for the determination of halogens were achieved using indium as the M component. In a preliminary communication,[212] the principle of mixing In^{3+} solutions with the samples and placing this mixture into the cavity was discussed. More precise data on the bands measured were reported in Reference 213, i.e., InCl-ME at 360 nm, InBr-ME at 375 nm, and InI-ME at 410 nm. The following detection limits were obtained: 2.5 ng Cl^- and Br^-, and 50 ng I^-. The mutual interference of halides and the influence of other anions was also studied. The techniques were applied to the determination of Cl^- in tap water[212] (compare also Reference 214).

It is also possible to determine pesticides which contain Cl or Br. The samples are oxidized in an oxygen flask. The halogen hydrides are collected in liquid ammonia. After separation by thin-layer chromatography, Cl and Br can be determined in indium-lined cavities.[216,217] The determination of phenol is possible after its bromination by InBr-ME.[218] This was used for the determination of phenol in lake water.

Recently the MECA was used for the chromatographic detection of organic Cl-containing compounds (chlorinated solvents and pesticides).[219] The absolute detection limit of this procedure was 1.2 ng Cl. This work was continued and expanded on InBr- and InI-MECA measurements.[220] It also used the stainless steel indium-lined cavity. Chloro-, bromo-, and iodo-alkanes were determined after GC separation.

c. Tin and Heavy Metals

Studies on SnH-, SnCl-, and SnBr-ME were carried out.[221] In the range 400 to 550 nm, the band maxima for SnCl molecules were observed at 440 nm and that for SnBr molecules at 495 nm (compare also Reference 183). The best way to determine tin by MECA is the conversion of tin to the volatile hydride. In an other paper,[222] the tin content of binary mixtures of tributyltinoxide and triphenyltin can be determined simultaneously, one after the other. In this case, the oxy cavity was used because it is necessary to form the SnO molecule.

Using the hydride technique it is possible to produce the SnH molecules and to determine tin compounds by SnH-ME.[223] Other special analytical application was not made (compare also Reference 209). Additional MX-ME signals were studied for their analytical potential.[224] In the course of the study, wide band emissions for MnX, CoX, NiX, PbX, and FeX molecules were found, which, unfortunately, were too weak for analytical application.[224] These studies resulted in the recommendation of InX-ME for X^- determinations.

Recently, other molecules were tried for analysis with MECA.[225] It could be shown that GeCl gives an emission at 455 nm in a carbon cavity in a hydrogen-nitrogen air flame. The emission of GaBr and GaI at 350 and 391 nm can be used for the determination of small amounts of Ga^{3+}, Br^-, or I^-. It was shown to also determine Tl molecules, but only the atomic emission of Tl at 377.5 nm was excited in the oxy cavity. There are also many matrix effects.

d. *Boron and Silicon*

Based on earlier research on the determination of B,[162-171] the possible application of the MECA technique to this element was studied (third paper).[215] It was found that with the use of boric acid in stainless steel cavities the well-known green emission is obtained. It was also found advantageous to extract the borate, as a complex, into MIBK. Within a range of 5 to 80 ng, linear intensity-concentration relations were obtained. It is also possible to introduce gaseous $B(OCH_3)_3$ with a N_2 stream into the cavity. The working range lies between 2 and 30 μg B. It is important in this case that a small quantity of O_2 be introduced into the cavity. This is a prerequisite for formation of the emitting BO_2. Recently, the determination of B was improved by combination of BO_2-MECA with an extraction method.[209] Borate was complexed with 2-ethylhexane-1,3 diol in MIBK. By using the oxygen-hydrogen flame, trace amounts of B can be determined. A further improvement was achieved by separation of the generated $B(OCH_3)_3$ in a trap at −50°C.[226] This procedure allows minimization of the background of methanol generated in the oxy cavity. Also with this procedure 50 ng of B can be determined.

Also in the oxy cavity it was possible to observe SiO-ME.[214] Recently silicon was determined after its conversion into silicontetrafluoride by sulfuric acid at 135°C. The gases are carried by nitrogen to an oxy cavity and the intensity of the SiO-ME was measured.[227] The method was used to determine silicon in an iron ore.

On the same basis, earlier a method of F^- determination was developed.[228] F^- amounts in the μg range were determined after its conversion to SiF_4 by SiO emisssion (see also below).

e. *Arsenium and Stibium*

The possibility of introduction of gaseous samples into the cavity was also utilized for determination of As and Sb by AsO- and SbO-ME at 400 nm and 355 nm, respectively. The hydrides of these elements were produced by reduction and introduced into the cavity with some O_2 (fourth paper).[229] There are, however, interferences (compare with References 209 and 228).

Recent studies on the determination of As, Sb, and B were made using the fluorides AsF_3, SbF_5, and BF_3, obtained by reaction of NaF and H_2SO_4 with the appropriate substances. The gaseous fluorides are introduced into a water-cooled cavity by a N_2 stream. The ME bands of the AsO, SbO, and BO_2 molecules are obtained[179] by excitation in a H_2-N_2 diffusion flame in the presence of some O_2. Problems were encountered with the simultaneous determination of As and Sb, as the wide ME bands of the AsO and SbO molecules are considerably overlapped. After separation of the hydrides (produced by reduction) by means of GC, appropriate determinations may be carried out (tenth paper).[231] Determinations are possible in the range of 5 to 50 μg/mℓ. If the hydrides are previously enriched using a cold trap technique, determinations are easily carried out in the range between 0.4 and 4 μg/mℓ. The combination of hydride generation with MECA was also used for the determination of As by other authors.[232]

f. Phosphorus

HPO-ME was also studied for applicability in the MECA technique. Using a cooled cavity, organophosphorous compounds could be determined by HPO-ME at 528 nm.[233] Recently phosphorus in organophosphorous compounds was determined after separation of such compounds by HPLC. The eluent was collected in cavities of a water-cooled duraluminium disc. The eluent of the HPLC is collected in the cavity and by stepwise rotation of the disc the HPO emission at 528 nm was measured.[234]

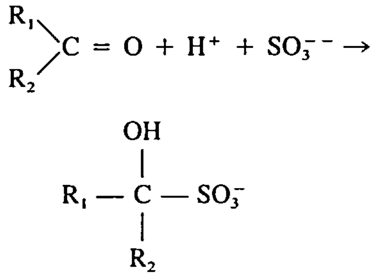
g. Nitrogen

Determination of N in nitrogeneous fertilizers is also possible using the MECA technique. In this case, the ammonia set free by alkali is introduced into the cavity with some O_2. The ME occurring at 500 nm is proportional to the N concentration.[235] This method was improved for the determination of ammonium nitrogen up to the parts per million range.[236] The ammonia was generated by sodium hydroxide; this was introduced by nitrogen into an oxy cavity and the NO emission at 500 nm was measured. Nitrate ions can also be determined after reduction to ammonia by Devarda's alloy. The method was successfully applied to the determination of ammonia in waters, sewage samples, and fertilizers.

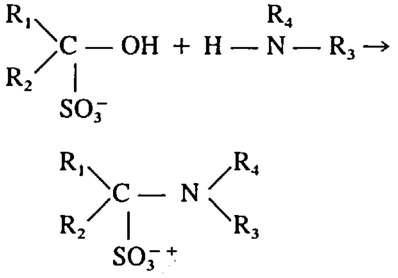
In a recent study, nitrate and nitrite were determined after reduction to nitrogen monoxide by iodide or zinc.[237] The emission of NO in an oxy cavity was measured at 526 nm. The hydrogen-nitrogen diffusion flame was used.

Organically bound nitrogen (e.g., aliphatic amines and amine acids) can be determined by an indirect procedure. The amines and amino acids react with carbon disulfide to their dithiocarbamates. After their formation, the sample can be directly introduced into the cavity and the S_2 emission is measured at 384 nm.[238]

Another procedure for the indirect determination of amines is described in Reference 239. The principle of this method is that the additive compound of carbonyls and sulfites reacts with amines:



(8)



(9)

Primary amines, hydrazines, and hydrazides react in the same manner. The S_2 emission was measured for the determination of the nitrogen-containing compounds.

h. Cadmium

As a final note, it may be mentioned that the easily vaporizable Cd atoms may also be determined in a stainless steel cavity by activation of Cd-AE over the range of 10 to 120 ng (seventh paper).[240] Atomic emission takes place at 326.1 nm. The determination is, however, reported to suffer interference by the presence of other cations like Fe^{3+}, Cr^{3+}, Mg^{2+}, and Sn^{2+}.

3. Conclusions

A general comparison of the MECA technique with the common flame technique described in Section VII.B is not possible as special experimental studies have not yet been performed. The analytical results obtained with the MECA technique are compiled in Table 5. A comparison of Tables 4 and 5 shows that the limits of detection by the two techniques are of the same order of magnitude. As to field application, it may be stated that the common flame technique is more frequently applied for practical analytical problems. As an alternative, many practical analytical problems were also solved by the MECA technique.

As an example we will mention that Gutsche and Rüdiger[241] developed a fluoride-specific detector for GC based on the MECA technique. The gas stream of the separated products from the gas chromatograph is introduced into the cavity through a capillary tube. Simultaneously, indium vapor, produced in a furnace heated to a temperature of 1233 K is introduced into the cavity. InF is formed in the cavity which is bound to organic compounds. InF radiates under these conditions at 233.7 nm and it is possible to detect 3.2 μg F if the excitation is carried out with a hotter H_2-O_2 flame. This example shows that co-workers who were working in the field of common flame technique also used MECA.

Last, but not least, it should be mentioned that the intensity of the works produced by the group of Townshend and Bogdanski resulted in a number of theses in which more details are described (see References 242 to 251).

D. Analytical Applications of MES Using Flameless Techniques

1. Excitation by Electrical Arcs

The advantage of the electric arc over many other sources of excitation is that solid substances may be evaporated directly into the arc plasma and excited to radiate. Since the temperatures of arc plasmas lie between 4000 and 8000 K, it is to be expected that only very stable molecules may occur at any significant concentrations. This accounts for the fact that only a few studies have been published on the direct use of ME in arc plasmas. Some attempts were made to utilize CaF-ME for determination of F^-.[252-255] A comprehensive study by Schoenfeldt[256] deals with the spectrographical determinations of F^- in standard rocks. For this purpose, 4 mg of the sample is mixed with 16 mg of a 1:2 mixture of $CaCO_3$ and C powder and excited in a DC arc at 7 A for 20 sec. The CaF molecule so formed emits in the plasma. The CaF-ME band at 529.1 nm is assessed in relation to an internal standard. The limit of detection is 100 ppm F, i.e., an absolute quantity of 400 ng F may be detected by this technique. Comprehensive studies on the evaporation of CaF for the analytical determination of F^- in rocks were carried out by Sugimae and Skogerboe.[257] Several types of electrodes and a number of substances were tested for their applicability as an internal standard (CaI: 526 nm; ScI: 535.6 nm; CaO: 609.7 nm; ScO: 607.9 nm). The limit of detection could be improved to 20 μg F/g of rock.

Recently, Radić-Perić and Perić and co-workers worked in the field of molecular emission of Ca- and F-containing plasmas.[258-261] They calculated the equilibrium composition of the gaseous system containing N, O, C, F, and Ca in a wide temperature range (298 to 7000 K). This gas mixture corresponds to a plasma of a DC arc freely

Table 5
ANALYTICAL APPLICATIONS OF MECA TECHNIQUE

Molecule	Dissociation energy (eV)	Band (max.) nm	Substance determined: ion/atom/compound	Detection limit	Combination with other methods/objects	Ref.
CuCl	3.6	526	Cl^-	ng	—	173
CuBr	3.4	488	Br^-	ng	—	173
CuI	3.0	509/11	I^-	ng	—	173
InCl	4.4	360	Cl^-	2.5—350 ng	—	189, 212, 213, 22
			Cl-R	2.5—40 ng	GC	191, 201
			Cl^-, Cl-R, pesticide	1.2 ng	GC	219, 230
			Cl^-, Cl-R	0.5 ppm		216,217
InBr	4.0	375	Br^-	2.5—40 ng	—	212, 213, 224
			Br-R	—	GC	201
			Br-R	10 mg/mℓ	GC	230
			Br^-, Br-R	0.5 ppm	—	216, 217
InI	3.4	410	I^-	50 ng	—	212, 213, 224
			I-R	—	GC	201
			I-R	15 mg/mℓ	GC	230
InCl	4.4	360	Phenol, pesticide	50 μmol	—	218
InF	5.4	233.7	F^-	3.2 μg	—	241
SnCl	4.2	440	Cl^-	—	—	221
SnBr	3.4	495	Br^-	—	—	221
SnH	2.7	485	Di-, tributyl-tin compound	—	—	222, 223
SnO	5.4	485	Sn-R, SnX_4 (Sn)	5—50 ng	—	222
S_2	4.4	384	SO_4^{2-}, S-R	10 ng	—	172
			SO_3^{2-}, SO_4^{2-}, S^{2-}, SCN^-, $S_2O_3^{2-}$	—	—	212
			SO_3^{2-}/SO_4^{2-}, simult.	—	—	184, 189
			$SCN^-/S^{2-}/S_2O_3^{2-}/SO_4^{2-}$ simult.	—	—	190
			SO_4^{--}	—	—	191
S_2	4.4	384	S	0.1%/coal	—	201
			S-R	10 pg	—	201
			SO_4^{2-}	0.01%, soil	—	192
			SO_4^{2-}	10 ng	—	193
			SO_3^{--}	0.5—6 μg drinks	—	198

			SO_4^{--}	30 ng dust	MECA-VAP	199
			SO_3^{--}/SO_2	5 ng	MECA-VAP	200
			Thiophen	5 ng/50 ppb	MECA-GC	202
			Methylthiophen, S^{2-}, SO_3^{--}	0.2 pg SO_3^{--}	MECA-GC	203
			S	40—90 μg in Se	—	204
			S, S^{2-}, SO_3^{--}, SO_4^{2-}	10—5000 ppm in solids	—	205
			Carbonyl compounds	ng	—	194
			Amino acids, amines	ng/μg range	—	238, 239
Se_2/SeO	3.4/4.4	411	Se-R, Se, SeO_2	0.4—4 μg	—	186, 187
			SeH_2	0.02—2 ppm	—	208
			SeO_3^{2-}, SeO_4^{2-}	1—15 ng	—	210
			Se	0.2—5 ppb	preconc.	211
			SeO_3^{2-}/SeH_2	7 μg	—	209
Te_2/TeO	2.7/3.9	500	Te, TeO_2	μg	—	186, 187
			H_4TeO_6	450 ng	—	210
NH_3	—	500	NH_3, NH_2-R, NH-R_2	1.5 μg N	GC	201, 227
NO	—	500	NH_4^+, NO_3^-	10 μg/ml	—	236
NO	—	526	NO_3^-, NO_2^-	0.5—300 μg N	—	237
HPO	—	528	P-R	—	—	233
			P-R	—	GC	201
			P-R	—	HPLC	234
AsO	6.1	400	AsH_3	—	Hydride tech.	229
		490	AsF_3	20—200 ng	NaF-sulf. acid	179
AsO	6.1	490	AsF_3	5—50 μg/ml	GC	231
			AsH_3, As-R	0.4—6 μg/ml	preconc.	201, 232
SbO	4.0	355	Sb-R	—	GC	201, 231
			SbH_3	—	Hydride tech.	229, 232
CH	3.4	431.5	C-H	—	GC	201
SiO	7.9	540	SiF_4	20—225 μg	NaF/H_2SO_4	179
		580	Si-R	2.5 μg Si/ml	GC	201
		540	SiO_2	0.2 μg	NaF/H_2SO_4	227
			F^-	10—300 μg	SiO_2/H_2SO_4	228
BO_2	—	518	BO_3^{3-}	5 ng B	Extraction	179, 215
			$B(OCH_3)_3$	2 μg B	—	179, 215, 226
			BF_3	50—300 μg B	NaF/H_2SO_4	179
			B-R	—	GC	201
GaCl	—	455	Ge	10—500 ng	—	225

Table 5 (continued)
ANALYTICAL APPLICATIONS OF MECA TECHNIQUE

Molecule	Dissociation energy (eV)	Band (max.) nm	Substance determined: ion/atom/compound	Detection limit	Combination with other methods/objects	Ref.
GaBr	4.3		Ga/Br	ng level	—	225
GaI	3.5		I	μg level	—	225
Tl atom		557	Tl	20—2000 ng	—	225
Cd atom		326.1	Cd	—	—	240

burning in air.[258] They also determined the radial temperature distribution and the distribution of line and band intensities of Ca, Ca^+, CaO, and CaF in a DC arc. In connection with the calculated values, it was possible to determine the radial distribution of the total Ca in the plasma with and without F. They showed that the formation of CaF lies in the arc periphery.[259] The optimum temperatures and radiative intensities for the emission of Ca, CaO, CaF, and CaF_2 were described.[260,261] Vilbanova[262] also described the determination of F traces by CaF emission. She found that a temperature of 3600 K which exists at a distance of about 10 mm from the arc axis is the best volume for CaF intensity. The determination limit was 1.1 ppm F relative to solids.

A technique used for the determination of nitrogen through CN-ME was developed by Dittrich and Abel.[263] It is well known that with the application of auxiliary C electrodes and excitation by the electric arc in air, the plasma temperatures are sufficient for the production of the CN radical from atmospheric nitrogen and the carbon of the electrode. This radical emits strong bands at 388.4 and 421 nm, which are often a disturbing background in emission spectroscopy. By burning the arc in a nitrogen-free argon or helium atmosphere, formation of the CN radical, and thus the emission, was prevented. If, under these conditions, nitrogeneous compounds (e.g., GaN/GaP and GaN/GaAs mixtures) mixed with spectrally pure carbon powder are placed in the carbon electrode under the thermal influence of the arc, according to:

$$GaN + C \rightarrow CN + Ga \tag{10}$$

the radical passes directly into the arc plasma of a permanent AC arc of 12 A and is excited to radiate. The CN-ME bands were evaluated at 388.4 nm with the reference to an internal standard (Sc_2O_3:ScI-AE:390.7 nm). With the most intense CN band, 500 ng N, i.e., 100 ppm N was referred to a sample of 5 mg, could be determined (compare with References 67 and 68).

Specific information on interference occurring in arcs by N_2- and CN-ME was given when P (214.3 nm), Mo (378.83 nm), and Pb (405.78 nm) were determined using a DC arc plasma and an echelle spectrometer. In the first case mentioned, the interference was reported to be caused by N_2 molecule, and in the second and third cases by the CN molecule.[264] Additionally, further studies were made on interferences[265] and on explanations of the mechanism of evaporation by studying ME.[266]

As mentioned previously, such interferences are caused by stable molecules such as CaF ($E_D = 5.5$ eV), CN ($E_D = 7.8$ to 8 eV), LaO ($E_D = 8.2$ eV), and N_2 ($E_D = 9.8$ eV).

2. *Excitation in Inductively Coupled Plasmas (ICP)*

Special determinations by excitation of molecular emission in the ICP have not been reported to date. Horlick[267] states that interferences occur with Mn-AE determinations at 275.4 nm due to NO- and OH-ME.

Bastiaans[268] described three sources that produced molecules in the ICP: impurities of the plasma gas, entrainment of the ambient into the plasma, and sample solution. Each source of molecules was found to produce a characteristic spatial distribution. This emission caused an enhancement of the background and also changed the line intensity when the appropriate atom takes part on the reaction. The same author[269] describes the radial distribution of OH emission intensity. The distribution of carbon-containing molecules in the ICP was also measured upon the addition of a hydrocarbon to the plasma. Also, Greenfield and McGeachin[270] showed that many molecules (CO, CN, C_2) exist in the plasma. Marquardt[271] found that molecules such as BeF emitted light in an argon ICP, but the intensity is too weak for analytical determination of F^-. Reeves et al.[272] found emission spectra of OH, NO, and NH molecules in the ICAP. They determined the intensity of the emission as a function of the height in the plasma, of input power, and environment. They carried out some experiments in the presence of salts forming stable oxide molecules and found emission bands of LuO and YO molecules. These molecules emitted especially in the "flame region" of the plasma in heights above 25 mm. Another type of molecular emission band was found by Rao et al.[273] They investigated the ICP in the far ultraviolet range and found, in the presence of the appropriate salts, such molecules as MgBr and SrF.

Up until the present, there have been no investigations with a direct analytical purpose. We also used the N_2^+ emission only for plasma-diagnostic purposes.[274]

3. Excitation in Microwave-Induced Plasmas (MIP)

Dagnall et al.[275] used an atmospheric argon MIP as an element-selective detector for GC; a detection limit of 4.5 ng Cl/sec was reported for the 257-nm chlorine molecular band. In another case, Alder et al.[276] described the determination of chloride traces in solution by argon-MIP emission spectrometry. The method is based on the evolution of chlorine from a potassium permanganate solution in sulfuric acid and measurements of the chlorine molecular emission at 257 nm. The detection limit is 10 ng chloride. Potential interfering elements are shown not to present any major problems.

C_2 bands in a MIP were detected by Hut and Jansen.[277] They used organic solvents such as methanol and chloroform and found the swan bands in a helium plasma. They combined this method with GC and LC and determined halogens by measuring atomic emission.

4. Excitation by Hollow Cathode Discharge

Because of the low plasma temperatures, the hollow cathode discharge is suited for the excitation of ME and, as a result, many spectroscopic studies have been carried out using this spectroscopic source (compare with Reference 52). Practical examples include studies of InF-[278] and GaF-ME.[279] These studies were, in most cases, not applied for analytical purposes, possibly because it is difficult to obtain reproducible conditions.

A paper on the determination of the Cl content in high boiling metals such as tungsten, tantalum, miobium, and molybdenum was published by Joffé and Korovin.[280] In the presence of Mg, the MgCl molecule may be produced in the hollow cathode, which subsequently emits at 377.9 nm. This emission serves for the determination of Cl. The mild conditions of this excitation may be recognized from the fact that MgCl has a dissociation energy of no more than 3.2 eV.

5. Excitation in Vapors of Electrothermally Heated Cuvettes

With the development of the so-called flameless AAS, wherein the samples are evaporated and atomized in electrothermally heated graphite tube cuvettes, the technique was also utilized in the emission mode. In the papers by Ottaway et al.,[281] methods of determining easily excitable metals with the use of the graphite tube cuvette emission were developed. As the vapor temperatures generated by these cuvettes are within the range of flame temperatures, the presence of free molecules and radicals may be expected. One paper offers a detailed report on the CN- and C_2-ME with atomization of Ca, Sr, and Mg salts.[282] Intensive CN-ME was found at 388.3, 387.1, and 386.2 nm when argon was used as a protective gas, and also at 621, 359.0, 358.6, and 356.6 nm when nitrogen was used as the protective gas. C_2-ME was observed at 516.5 and 512.9 nm. In the presence of metallic salts, specific MO-ME was also observed; CaO-ME at 370 to 450 nm, 545 to 560 nm, and 590 to 650 nm. These wide bands were structured and had some maxima. The SrO (possibly SrOH)-ME at 606.4 nm and the MgO-ME between 375 and 382 nm were also observed. If some hydrogen was added to the shielding gas, however, the MO-ME was depressed by reduction of the MO concentrations.[283] There are but few special applications of graphite tube cuvettes for determination of nonmetals by ME. Gutsche et al.[284] report the application of micrographite tube cuvettes for the specific determination of Br by InBr-ME at 372.7 nm in the separate fractions of the effluent from a gas chromatograph. According to this technique, an indium-coated Cu/Be plate is directly inserted in a graphite tube cuvette (Mini-Massman type). The Br-containing organic compounds coming from the gas chromatograph are led through this heated tube. Bromine forms the InBr molecule with indium. Directly above the vertical graphite tube the InBr-ME is measured. The limits of detection lie between 5 and 50 ng Br, depending on the organic compound. In another paper,[285] this technique was applied to the specific determination of Cl by InCl-ME at 359.9 nm. The limits of detection lie between 1.3 and 48 ng Cl, depending on the organic compound. It is stated in these papers that when these cuvettes are applied the dynamic range is greater than that obtained with the flame interference filter detector 132 a; it amounts to almost three orders of magnitude greater.

It may be summarized that ME with electrothermally heated cuvettes has very rarely been applied for analysis. An advantage of this method, however, is that commercially available instrumentation may be used. A survey of the analytical results of the technique dealt with in Section IV.D is given in Table 6.

V. MOLECULAR ABSORPTION SPECTROMETRY (MAS) OF DIATOMIC MOLECULES

A. General Aspects

For reasons similar to those stated above under Section IV. A, the first studies on molecular absorption (MA) were carried out in flames. The reasons are as follows:

1. Because of the low temperatures, high molecular concentrations occur in flames.
2. The development of AAS, which is a forerunner of this technique, began with the almost exclusive use of flames.
3. Interferences by band absorptions observed in the flame-AAS had to be elucidated. Interferences due to molecular absorption in electrothermal-AAS were also encountered. Therefore, studies were also extended to this field.

The basic principle governing the analytical applications agree with those mentioned in Section IV. A.

B. Analytical Significance and Application of MAS Using Flames

1. Significance of MAS for the Explanation of Interferences in Flame AAS

Molecule formation may have a direct effect on the AA signal of the analyte due to reduction of the atom concentration (compare with Table 1). It must be considered that molecule formation takes place primarily between the analyte and the flame gas or matrix atoms present in excess concentrations. Furthermore, molecules of flame gases or the matrix may increase the background considerably by nonspecific MA. It is common practice to decrease or remove the nonspecific background by means of one of four well-known compensation procedures (two-line method, deuterium lamp background correction, Zeeman-AAS, and the Smith-Hieftje system). Consequently, in monographs of AAS these problems of MA are often considered (compare with Reference 286). Concrete data concerning the problem may also be found in a few original papers (see below). Thus, it was found that CaOH-MA which occurs between 558 and 550 nm overlaps with the Ba resonance line at 553.6 nm, producing interference in the Ba-AA.[287] Koirtyohann and Pickett[288,289] studied the absorption caused by alkali and alkaline earths when a long tube absorption system was used. They found

Table 6
ANALYTICAL APPLICATIONS OF MOLECULAR EMISSION IN ELECTRONICALLY GENERATED PLASMAS

Molecule	Dissociation energy (eV)	Band (max.) nm	Type of plasma	Substance determined: ion/atom/compound	Detection limit	Interferences	Ref.
CaF	5.5	529.1	arc	F^-	400 ng	—	256
		529.3	arc	F^-	20 μg/g solid	—	257
		529.3	arc	F^-	1.1 ppm/solid	—	262
CN	7.8—8.0	388.4	arc	N	500 ng	—	263
N_2	9.8	—	arc	—	—	P	264
LaO	8.2	—	arc	—	—	La	265
CN	7.8—8.0	388.4	arc	—	—	Pb, Mo	264
NO	6.5	—	ICP	—	—	Mn	267
OH	4.4	—	ICP	—	—	Mn	267
Cl_2	2.5	257	MIP	Cl-R	4.5 ng (GC)	—	275
Cl_2	2.5	257	MIP	Cl^-	10 ng	—	276
InF	5.4	—	HCL	—	—	—	278
GaF	6.0	—	HCL	—	—	—	279
MgCl	3.2	377.9	HCL	Cl^-	—	—	280
CN	7.8—8.0	388.4	CFA	—	—	Ca	282, 283
C_2	6.1	516.5	CFA	—	—	Ca	282, 283
CaO	4.0	590—650	CFA	—	—	Sr	282, 283
SrO	4.3	606.4	CFA	—	—	Mg	282, 283
MgO	3.5	375—382	CFA	—	—	—	282, 283
InBr	4.0	372.7	CFA	Br-R	1—50 ng	combination/GC	284
InCl	4.4	359.9	CFA	Cl-R	1—50 ng	combination/GC	285

Note: ICP = inductively coupled plasma; HCL = hollow cathode lamp; CFA = carbon furnace atomizer; MIP = microwave-induced plasma.

that wide MA bands occur between 640 and 680 nm from SrO molecules, between 550 and 560 nm from CaOH molecules, between 230 and 300 nm from KBr molecules, and between 300 and 400 nm and 220 and 280 nm from KI molecules.

Very early reports are also found on the suppression of Ga- and In-AA signals in C_2H_2-N_2O flames by HCl caused by formation of stable GaCl and InCl molecules, respectively.[290] Subsequently, a team of Japanese researchers lead by Haraguchi and Fuwa intensively investigated such problems. In 1972, two papers were published.[291,292] It was found that PO-MA occurs in the range 230 to 250 nm with a peak at 246 nm when 1 M H_3PO_4 is aspirated into flames.[291] The second paper dealt with indium.[292] When a solution consisting of 0.2 M In^{3+} and 2 M HCl was atomized in a C_2H_2 air flame, InCl-MA was obtained between 263 and 270 nm with a peak at 267.2 nm, representing the C band system of the InCl molecule. The increased background in the range 260 to 300 nm was assigned to the InO molecule. It was later determined that InCl molecules occur not only as a result of incomplete dissociation in the flames, but that they also form in the flames. InCl-MA was also observed when an In^{3+}/ClO_4^- solution was atomized.[293] SO_2-MA has also been reported[294] (compare with Section V. E, see below), particularly in long tube absorption systems. The peak of the SO_2-MA occurs at 207 nm.[295] S determinations have also been successfully made based on MA of triatomic SO_2. For this purpose, the emission of the Mg hollow cathode lamp at 202.5 nm was utilized. In the spectral regions 280 to 290 nm and 305 to 320 nm, strong OH bands occur as background interferences and a new principle of background correction[296] was suggested using two flames of the same type to deal with this problem.

In spite of the relatively good thermal homogeneity of the flame plasma, it was expected that the distribution of molecules and atoms would be different for the two flames. Distribution profiles were measured for the C_2H_2-N_2O flame for a number of metal atoms and for OH radicals.[297,298] Conclusions concerning the mechanism of atomization were drawn based on observed relations between the MO molecule formation and the MO molecule reduction by C atoms.

In addition to the species already mentioned, MA of the following molecules has been measured: InF, InBr, AlF, AlCl, and AlO.[299] Molecular interaction of indium in the presence of HBr, HCl, and $HClO_4$ was studied in detail.[300] InCl and InBr molecules were detected by their MA. Studies on the mechanism of atomization of indium and copper were carried out by measurement of the distribution of the In and Cu atoms in the flames in the presence of several acids.[301] By assessing relationships between the atom distribution and the dissociation energies of the molecules, further advances were made in elucidation of this mechanism.[301] A survey of the MA spectra obtained for In-containing diatomic molecules (InCl, InF, InBr) is given in Reference 302. Apart from the characteristic peaks of the C-band system of these molecules there are weak bands between 205 and 215 nm, which were assigned to the NO molecule. Nakahara and Musha[303] studied In-AA in cool H_2-N_2 and H_2-Ar diffusion flames. They found InH-MA at 399.3 and 454.1 nm and InCl MA at 267.2 nm. Additionally, InI-ME at 399.3 nm, InBr-ME at 372.7 nm, and InCl-ME at 359.9 nm were observed in solutions of adequate concentration. This served as a confirmation of the studies of Haraguchi and Fuwa.

A useful apparatus for the study of MA spectra was described by Haraguchi et al.,[304] who developed an analog data processing system which served to correct for wideband or continuous background absorption. The apparatus was tested when the PO-, InCl-, and Mg-MA were recorded.

Later, Sr-containing solutions were studied for their MA spectra.[305] Depending on the composition of the solutions, emission bands of the SrO and SrOH molecules were observed between 360 and 400 nm and between 580 and 700 nm, respectively. Both bands were also observed in absorption. In Cl-containing solutions, SrCl-ME was detected at 638 nm. SrCl- and SrBr-MA bands, which did not occur in emission, were found at 220 and 250 nm, respectively. This is probably a case of photodissociation. These studies were continued with the elucidation of the alkalihalide MA in C_2H_2 air flames.[307] The following bands were obtained: NaCl, 235 nm; NaBr, 275 nm; NaI, 330 nm; KCl, 245 nm; KBr, 275 nm; KI, 328 nm; RbCl, 250 nm; RbBr, 280 nm; RbI, 330 nm; CsCl; 245 nm; CsBr, 268 nm, and CsI, 325 nm. In the case of Li-containing solutions only the LiO-MA band at 265 nm was found. All bands observed were relatively wide and were attributed to photodissociations (compare with Reference 205). In this context, special studies on background correction have also been published. Höhne and Jackwerth[308] have found that the InCl-MA band at 267 nm has a fine structure which directly interferes with Au-AA. None of the usual compensation procedures succeeds in correcting for the influence so that systematic errors can occur (compare with Section V. C).

Effects were also made to reduce the background with the use of special flames. In a C_2H_2-N_2O flame, Kawamura[309] reduced the interference by CaOH-MA on Ba-AA using N_2 as a flame shielding gas. Fry and Denton[310] studied the MA spectra of complex matrices in premixed flames and electrothermal atomizers (compare with Section V. C). MA by NaCl and MgO molecules was found.

At present, Daidoji[311-313] is working in the field of molecular absorption using flames. In C_2H_2 air flames and argon-hydrogen air flames, he detected independent from the composition of solutions such molecules as NaCl, NaOH, PO, NO, and SO_2.[311]

In another paper, the molecular absorption of Ga species was studied. The following molecules were found: GaOH, GaCl. By measuring the molecular absorption of GaCl at 249 nm, GaOH at 241 nm, and Ga at 294.3 nm, the total concentration of Ga in flames was calculated. The distribution of these species independent from the hydrogen flow rate in some positions of the flame was measured.[312] In the same manner, the molecular absorption of manganese, vanadin, chromium, molybdenum, and tungsten salts in flames[313] was investigated. The maximum absorption of these band spectra were obtained at 256 and 375 nm for manganese, 293.4 and 297.6 nm for chromium, 242.5 and 344.7 nm for molybdenum, and 243.7 and 302.3 nm for vanadin. These bands coincide with the appropriate emission bands. Many spectral interferences by these bands were described.

2. Quantitative Determinations of Nonmetals by MAS in Flames

The above studies of MA bands of di- and triatomic molecules have been applied to the analytical determination of nonmetals only to a small extent.

A paper on the determination of SO_2 at 207 nm was published as early as 1969.[295] When an absorption tube was used, 10 μg S/mℓ were detected in H_2 air flames. Later, an attempt was made to determine PO_4^{3-} ions by PO-MA at 246 nm. Using a C_2H_2-N_2O flame, a detection limit of 20 μg P/mℓ could be obtained.[314] Table 7 gives a summary of the results.

C. Analytical Significance and Application of MAS using Gases and Electrothermally Generated Vapors

1. Significance of MAS on the Explanation of Interferences in AAS with Electrothermal Atomization

The development of AAS with electrothermal atomization was initiated by the studies of L'vov[315] in 1961 and continued by Massmann in 1968.[316] Due to the extraordinarily good absolute detection limits (picogram range) and the possibility of using microsamples, this technique has become over the last decade the leading technique for

Table 7
ANALYTICAL APPLICATION OF MOLECULAR ABSORPTION IN FLAMES AND GASES

Molecule	Dissociation energy (eV)	Band (max.) nm	Absorption	Substance determined: ion/atom/compound	Detection limit	Ref.
SO_2	—	207	H_2-air-flame	SO_3^{2-}	10 μg S/mℓ	294
PO	—	246	C_2H_2-N_2O-flame	PO_4^{3-}	20 μg P/mℓ	314
SO_2	—	200 — 230	Cold gas tube	SO_3^{2-}, wine	3 μg/mℓ	388
SO_2	—	200 — 230	Cold gas tube	SO_2	20 μg	372, 373
			Cold gas tube	SO_2	5 ng	389
H_2S	—	194 — 200	Cold gas tube	S^{2-}	1.2 μg S/mℓ	377
					50 ng S/mℓ	383
					1 ng S	389
Br_2	2.0	410	Cold gas tube	Br^-	7 μg/mℓ	376
I_2	—	530	Cold gas tube	I^-	4 μg/mℓ	376
NH_3	—	201	Cold gas tube	NH_4^+	1 μg N	380
				NH_3	0.1 μg N/mℓ	382
				NO_3^-	1 μg N/mℓ	381
				NH_4^+	0.5 μg N/mℓ	389
				NH_4^+	20 ng/mℓ	395, 396
		197.2	Cold gas tube	NH_4^+	0.1 μg	394
		201	Cold gas tube	NH_4^+, CN^-, NO_2^-	30 μg CN^-/mℓ	386, 387
NOCl	—	195	Cold gas tube	NO_2^-	200 ng	385
NO	6.5	236.4	Cold gas tube	NO_2^-	0.04 ppm	389

determination of individual elements in the range of traces and extreme traces. Because of the initially great success, systematic studies of interferences, etc. were hardly carried out over the first few years. It became apparent very soon, however, that both the signals and the background were strongly affected by the matrix and the parameters of vapor generation. Of particular importance is the fact that there is a negative temperature gradient between the sample holder (graphite tube) and the vapor. Due to the former, in particular, the rate of heating plays an important role; due to the second peculiarity, the interferences mentioned in Table 1, i.e., molecule formation and condensation, may arise (compare with Reference 356). After L'vov[317] and Takeuchi et al.[318] had published the first data on MA by KI in graphite tube cuvettes and tantalum ribbon atomizers, comprehensive data on the occurrence of stray light and dissociation continua of alkali halides (NaCl, NaBr, NaI) and sodium sulfate during their evaporation in graphite tube cuvettes were published at the 17th CSI 1973 in Florence by Gücer and Massmann.[319] There are also reports on dissociation continua of the SO_3 molecule and bands of the SO_2 molecule.[319] Furthermore, it was found that the use of N_2 as a purge gas in combination with cuvette temperatures of about 2600 K produces strong CN-MA bands at 388.3, 387.1, and 386.2 nm. This means that reactions of the nitrogen with the carbon of the graphite tube to form CN radicals are possible under the conditions mentioned. A survey summarizing these results was published somewhat later.[320] In this paper, the occurrence of C_2- and CN-ME was mentioned (compare with Section IV. D). The neccessity to compenstate for these background phenomena, which are caused by molecules, is pointed out.

Similarly, at the 17th CSI, Welz[321] reported correlations and thermal data of substances and appearance temperatures of AA signals. He succeeded in providing information on the mechanism of evaporation of certain salts and showing that molecules like $FeCl_2$, FeS, etc. played a role in this process. These two papers outlined two interference variables — those affecting the signals as well as the backgound.

Further studies of this problem, which were always closely connected with spectroscopic aspects, followed. Because of the close relations between the two interference variables, it is not possible to deal with them in separate sections.

Culver and Surles[322] extended the studies on the MA of alkali halides. They found the following MA bands: KCl, 246 nm; NaCl, 235 nm; KBr, 210, 255, and 278 nm; NaI, 220, 257, and 325nm; NaF, 215 nm; and $CdCl_2$-MA at 214 nm. Only a few micrograms of these substances cause absorbance between 0.5 and 1 nm in graphite tube cuvettes. Pritchard and Reeves[323] also studied the formation of molecules of alkali halides. These authors discuss charge transfer transition and maintain that the KBr-MA band at 212 nm may arise as a result of an ionization process of K. Calculations of the dissociation energies of the alkali halides were carried out as well.[324] Ottaway[325] gives a survey of atomization processes and interferences. Krasowski and Copeland[326] investigated the matrix interference of some alkali salts on Cd-, Cu-, Cr-, and Pb-AA. They found independence of the concentration of alkali salts band spectra, which caused the interference.

Yasuda and Kakiyama[327] studied the atomization characteristics of a number of heavy metals. They found a number of molecular absorption bands which they tried to assign to various species. In particular, the MA bands of the halides were found. In this way MAS helped to elucidate the atomization processes in AAS. A second paper[328] gives a report of the evaporation of Cd, Zn, and Pb. MA spectra were obtained for $PbCl_2$, $PbBr_2$, and also for halide salts of Zn and Cd. There were no definite assignments to specific molecules.

Based on the fact that molecules exist in the vapor generated in graphite tube cuvettes, Frech and Cedergren[329] initiated calculations of the concentrations of various species as a function of (if possible) all components in the vapor, its boundaries (graphite tube), and the thermodynamic properties of the substances. Initially, studies on the atomization of Pb and Fe as well as Pb and Fe molecular formation were carried out. This helped to explain Pb-AA interferences which occur in the presence of Cl^- ions and which could be eliminated by addition of H_2 to the purge gas.[330,331] In the presence of H_2, HCl is liberated from Cl-containing species. The HCl molecules escape from the system before the atomization phase. This is an application of chemical matrix modification techniques in graphite tube cuvettes.

Another example of matrix modification is given by addition of NH_4NO_3. The following transformation occurs in the graphite tube cuvette:

$$NH_4NO_3 + NaCl \rightarrow NaNO_3 + NH_4Cl \qquad (11)$$

The resulting ammonium chloride is easily volatilized and escapes before the atomization process. Application of this technique enables direct determination of heavy metals in sea water using AAS,[331] as both the background MA and Pb-AA interference are suppressed. These studies were later continued with Al. The concentrations of the molecules AlO, Al_2O, AlN, AlCl, and AlS were calculated from thermodynamic data and the vapor composition given as a function of temperature.[332] These calculations were checked by experiments. The conclusion was made that the most favorable conditions for a high atom concentration occur if high ashing temperatures are applied to remove nonmetallic substances.[332] Another method of removing Cl^- interferences in the determination of Al by AA is addition of EDTA.[334] With addition of EDTA the Cl^- ion is removed from the coordination sphere of Al in the aqueous phase.

In the course of our studies on the trace analysis in A^{III} B^{V}-semiconductor systems, we found [335] that, depending on the medium, very extensive MA bands of Ga- and In-containing species occurred in graphite tube cuvettes. In the presence of HNO_3, GaO-MA was observed between 235 and 270 nm and two InO bands were observed between 270 and 310 nm and 215 and 240 nm. In the presence of HCl, the GaCl-MA band and the InCl-MA band occurred with peaks at 248.3 and 267.2 nm, respectively. Additionally, the PO-MA band was found at 246 nm and an AsO-MA band was observed in the range between 200 and 230 nm. The matrices which had a complex composition of $A^{III}B^{V}$ showed the appropriate complicated molecular absorption spectra, which caused a background interference problem in trace analaysis.

The molecule formation found here also had a great influence on the trace analysis of indium and gallium by AAS.[336] In the presence of HCl, a considerable signal depression occurred as compared with the measurements in HNO_3, which may be ascribed to formation of the stable diatomic molecules GaCl and InCl in the vapor of the graphite tube cuvette. These studies were continued using other matrices such as HNO_3, HCl, HBr, MIBK extracts, $CHCl_3$ extracts, etc.[337,338] By systematically studying analyte evaporation as a function of various thermal and chemical parameters, it could be shown with the help of MAS that the GaCl-, InCl-, InBr-, and also the GaO- and InO-MA signals increased whenever the Ga-A and In-AA signals, respectively, decreased. This was direct evidence that the depression of Ga- and In-AA signals cannot be ascribed to early volatilization of highly volatile compounds, but to formation of stable GaCl, InCl, and InBr molecules. The fact that large signal depressions occurred in AA, particularly in the presence of halogenated hydrocarbons, was found by Tölg et al.,[339] when they studied systematic errors in the AAS determination of Fe, Cd, Co, Ni, and As. It was also postulated that molecule formation was responsible for the depression. Additionally, in the case of gallium and indium, depression was caused by these substances because of molecule formation.

Further studies by us showed that in the presence of a large excess of anionic components, less stable molecules may also form. Cadmium, zinc, and manganese salts produce the same AA signals whether they are dissolved in HCl or HNO_3 because the corresponding MCl molecules are rather unstable.[340] If, however, the Cl concentration present in the atomization phase is increased by the presence of an inorganic chloride, e.g., $GaCl_3 \times n\ H_2O$, signal depressions occurs in Zn-, Cd-, and Mn-AAS. By varying the thermal parameters and the chemical composition it was shown that it was indeed the formation of molecules between the metal atoms and the Cl atoms that was the reason for the signal depression.[341] Ottaway et al.[342] obtained a similar result. By separately dotting selected components into the graphite tube cuvettes and measuring the same AA depressions, it was concluded that molecule formation occurs in the vapor phase, this being the reason for AA interferences. A similar result was obtained by Katz and Taitel[343] in the determination of Li^+ in the presence of $CaCl_2$ by AAS, signals occur due to formation of LiCl molecules. If, however, the substances are released from the excess Cl^- by treating with sulfuric acid, suppression of Li-AA signals is not observed. Other researchers have also studied the MA of various species as an aid to elucidating the mechanism of vaporization in AAS. Sedych and Beljaev[344] studied the evaporation of Sr in a graphite tube cuvette and found SrO molecules as well as SrCl molecules particpate in the vaporization process. In similar studies on Te-AA, $TeCl_2$ was found to evaporate as $TeCl_2$ in the presence of HCl and as TeO in the presence of HNO_3.[345] The same authors found that both PbCl and PbO molecules may be formed when Pb is atomized.[346,347] Removal of the depressive interferences caused by Cl ions is possible when the sample is treated with HNO_3/HF mixtures.

Similar practical problems were also solved by other researchers. Manning and Slavin[348,349] determined Pb in a Cl matrix following addition of $MgCl_2$ (see Equation 11).

Czobzik and Matousek carried out studies on the atomization of Pb and Cu from Cl matrices.[350] By optimizing thermal parameters and addition of matrix modifiers, they succeeded in removing the interference caused by Cl^-.

In a comparison between pulsed type atomization and constant temperature electrothermal atomization, the influence of various chlorides on Mn-AAS was studied.[351] Eklund and Holcombe found signal depressions in Cu-, Au-, Ga-, and Ca-AA in the presence of NO_3^- and SO_4^{2-}, presumably caused by molecule formation.[352] Further studies showed that kinetics play a decisive role in the formation of molecules and the resulting interferences.[353]

L'vov has also made intensive studies on the formation of molecules in electrothermally generated vapors. It was found that, apart from the formation of stable diatomic molecules involving the halides, formation of triatomic molecules with pseudohalide CN plays an important role. The dissociation energies of the cyanides are of the same order of magnitude as those of the fluorides.[354] Comprehensive studies were made with cerium. It was found that CeO molecules are almost completely dissociated in graphite tube cuvettes, whereas CeCN and CeC_2 molecules are only partically dissociated.[355] The dissociation energies of the alkaline earth cyanides were determined. The strongest MA bands were also determined: CaCN-MA: 608 to 643 nm, E_D: 6.0 eV.[356] These studies were extended to the rare earths and their cyanides[357] and also the alkali cyanides.[358] With the rare earths, the dissociation energies lie between 5.2 eV for the YbCN molecule and 6.3 eV for the LaCN molecule. The data with alkali cyanides are as follows: LiCN: 5.9 eV; NaCN: 5.1 eV; KCN: 5.4 eV; RbCN: 5.3 eV; and CsCN: 5.5 eV.

Also the spectrum of AlCN was observed in nitrogen atomosphere in the range of 250 to 290 nm.[359] This spectrum has been similar to the spectra of alkaline earth monocyanides. The distances between spectral maxima are in agreement with calculated frequency of stretching vibrations of the Al-C bond in the AlCN molecule. In argon atmosphere, the spectra of Al_2C_2 appears. These investigations were extended to some heavy metals.[360] Atomization energies of halides and cyanides of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn were determined. The same was done for DyC_2[361] A survey about thermodynamic studies of gaseous monocyanides by electrothermal atomic absorption spectrometry was published by L'vov and Pelieva.[362]

Recently, Sedych et al.[363] investigated matrix interferences in Ag-, Te-, Pb-, Co-, and Ni-AA in the presence of some metal nitrates and metal chlorides. In all casese, the metal chlorides interfered more strongly, which was caused by the formation of gaseous halides. A survey of these investigation is in preparation.[364] Kitagawa et al.[365] determined the dissociation of Cu species by measurement of the Cu-AA and the CuCl molecular emission. Wendl and Müller-Vogt found that the volatilization of the suboxides of Sn and Ge and the nonatomizable SiC reduce the absorption signal of these elements.[366]

It could be shown by Gücer and Berndt[367] that also by application of a Pt-loop atomizer there exist some molecules in the plasma (e.g., NaCl, NaI, etc.). They found that the background is strongly reduced (400 times) in comparison to tubes. Rayleigh scattering was negligible.

Lately, we investigated some interference effects in $A^{III}B^{V}$-semiconductor analysis. We could show that there exists for Ag, Bi, Cd, Sn, and Tl, in the presence of hydrochloric acid and metal chlorides such as $InCl_3$ and $GaCl_3$, strong AA signal depressions. These depressions could be explained by formation of AgCl, BiCl, CdCl, and TlCl molecules.[368] The reason for the strong signal depression of Ge-AAS and Sn-AAS in the presence of sulfuric acid could be explained by us by formation of the very stable SnS and GeS molecules.[369]

Also, in the hydride technique there exist interference effects caused by molecule formation. We could show that, e.g., the AsSb molecule is formed in the vapor of the heated quartz cuvette of hydride apparatus. By changing the atomizers and using a graphite tube for the atomization of the hydrides, the interference effects of Sb on As-AA and As in Sb-AA decreased. With the enhancement of the temperature up to 2400 K,[370] here is evidence for the formation of such molecules. Besides this, we detected this molecule spectroscopically in the vapor.

A very comprehensive survey of all problems that may occur in electrothermal atomization was published by Sturgeon and Chakrabarti,[371]

It may be summarized that molecule formation is of greatest significance in electrothermal atomization. Molecules may be directly formed from the matrix components as well as from interaction of the analyte and the matrix. The former results in an increase of background, the latter in depression of the signal. For removal of such interferences, chemical additions may be used under optimal thermal conditions, the aim always being to produce separations of the molecule-forming components within the graphite tube cuvette prior to or during atomization. Studies of MAS have also been used for determination of molecular concentrations in vapors, for elucidation of atomization mechanisms, and for the determination of thermal data such as dissociation energies.

2. Quantitative Determination of Nonmetals in Gases by MAS

Studies on the possibility of applying MAS for analytical determinations in cool systems were carried out in most cases by two research teams. Syty and co-workers[372,373,376,377,385-388] and Cresser and co-workers[378-384] used cold vapor techniques, i.e., they studied the MA of gases and of substances which may be transformed into the gas phase at rather low temperatures. It was Cresser who coined the term gas-phase molecular absorption spectrometry (GPMAS). Despite the fact that this frequently concerns the MA of polyatomic molecules, these techniques shall be mentioned here because of their basic similarity to the other methods dealt with in this paper.

The first papers by Cresser[379,380] dealt with the analysis of SO_2 by MA using the bands between 320 and 360 nm (compare with Reference 381) and 200 and 230 nm (compare with Reference 382); 20 μg SO_2 were detected in the absorption tube. Determination of SO_2 in air and sulfite in solution was carried out. In the latter case, SO_2 was removed by acids. In another case,[383] information on the determination of Br^- and I^- ions by Br_2- and I_2-MA is provided. From appropriate solutions of the halides, the halogens are set free by addition of V_2O_5/H_2SO_4, $KMnO_4/H_2SO_4$, or $K_2Cr_2O_7/H_2SO_4$ and removed from solution by a gas stream. In an absorption tube I_2-MA was measured at 530 nm and Br_2-MA at 410 nm. The best detection limits obtained are 4.1 μg I^-/mℓ and 7 μg Br^-/mℓ, depending on the oxidation system. Recently, another paper was published[384] concerned with the determination of S^{2-} by H_2S-MA. H_2S absorbs between 180 and 250 nm with some peaks between 194 and 200 nm. The technique is the same as that described above, i.e., H_2S is set free by acids and removed in a gas stream; 1.2 μg S_2^-/mℓ may be detected.

The determination of nitrite ions is possible by NOCl molecular absorption at 195 nm.[385] A detection limit of 200 ng NO_2^- was obtained. The directed termination of NH_3 was also described.[386] In similar manner, the direct and precise determination of cyanide is possible.[387] The formed cyanate was hydrolyzed by concentrated H_2SO_4 to NH_3. After alkalization of the solution, the GPMAS of NH_3 was measured (compare with Reference 386); 1.4 μg CN^-/mℓ can be detected relative to 2 criterion. The real determination limit is given for 30 μg CN^-/mℓ.

A practical result of these techniques is given for the SO_2-GPMAS.[388] In table wines, sulfur dioxide was determined. It determined the free SO_2 and after treatment of alkalines to the wine, the bound SO_2 could be determined. The dectection limit was 3 μg SO_2 per milliliter of wine.

Syty began his studies with a preliminary paper in 1976[372] on the possiblilty of applying GPMAS to the determinations of anions in solutions. Absorption bands for SO_2 and H_2S were measured between 185 and 220 nm and for NO_2 between 300 and 550 nm. The studies were extended to the NH_3 molecule.[373] NH_3-MA bands occur between 195 and 225 nm with peaks at 201, 205, and 212 nm. For absorption measurements, an absorption tube of 100 mm in length was used. These studies were applied to several analyses. The possibility of determining NH_3[374] was also utilized for determination of the NO_3^-.[375] In this procedure, the NO_3^- ion must first be reduced to NH_3 by Ti^{3+}; 1 μg N/mℓ may be detected with 10-mℓ samples. Another paper[376] is concerned with sulfide determination by H_2S-GPMAS. Determinations may be carried out in the range between 0.1 and 100 μg S/mℓ. H_2S is removed from the solutions by HCl. The detection limit is 0.05 μg S/mℓ with 20-mℓ samples. Recently, a survey of these results and some procedural improvements was published.[377] By using an absorption tube of 530 mm-lengths, the detection limit could be improved to 0.1 μg N/mℓ. The application of this principle to the determination of aminocarboxylic acids such as leucine, phenylalanine, and others between 0 and 50 μg/mℓ is reported. Problems of SO_2-MA, H_2S-MA, and NO_2 determination by NO_2-MA are also dealt with. Another survey was published in the European spectroscopy news.[378]

Recently, Pleskai[389] reported an improvement of this technique, which is characterized by the application of a much more intense spectral light source (as compared with continuum light sources) such as electrodeless HF discharge lamps of As, Se, Sb, and Pb. The following detection limits were reported: NH_3, 0.5 to 10 μg; H_2S, 0.001 to 1 μg; and SO_2, 0.005 to 2 μg. NO-MA was also measured using an EDL filled with N_2O_3/N_2.[390] MA bands were found at 214.9, 204.7, 226.3, and 236.4 nm. The detection limits for the NO molecule are reported to be 0.04 ppm at 236.3 nm if an absorption tube of 300 mm is used.

In recent studies, some other scientists used the GPMAS for the determination of

NH_3 in some matrices.[391-393] Vijan and Wood[394] determined NH_3 by GPMAS at 197.2 nm using a hot quartz tube; the detection limit was 0.1 μg/mℓ. Takahashi et al.[395] improved the sensitivity of the determination of free NH_3 by GPMAS. They trapped the generated NH_3 in a stainless steel tube cooled with liquid nitrogen. Then the NH_3 was introduced into an absorption tube with a length of 1000 mm. The sensitivity relative to 0.0043 absorbance was 20 ng N/mℓ. The method was used for analytical determinations of NH_3 in soil extracts. McPherson[396] also described a method for NH_3 determination in urine with an accumulation step in solution. Table 7 gives a survey of the results.

3. Quantitative Determination of Nonmetals by MAS in Electrothermally Generated Vapors of Graphite Tube Cuvettes

Parallel and independent studies on the use of electrothermally heated graphite tube cuvettes for the determination of nonmetals by MAS were undertaken in our laboratory and in those of Haraguchi and Fuwa. In an analogy of the abbreviation AAS with electrothermal evaporation (etv), the abbreviation MAS with etv was introduced by us.[397]

In both laboratories the results gained from the studies of AA interferences (compare with Sections V.B.1 and V.C.1) led to the conclusion that the intense MA by various diatomic molecules and radicals ought to be of some value for analysis.

We believe that application of MA might be of some advantage as compared with the technique of ME:

1. In the very transparent rare gas vapors generally used in AAS, MA may be observed more easily than ME, as the transfer of chemical energy from radical recombinations is only possible to a small extent.
2. In contrast to ME, no thermal energy is necessary for the excitation of MA; thus the vapor temperature may be lowered to the point where vaporization can just be insured.
3. It may be expected that MAS studies are also possible in the UV where ME is very weak due to the high excitation energies required.
4. A further advantage, also shared by the MECA technique, is that microsamples may be used.

Surveys on these techniques are given in References 67, 68, and 397 to 399. The procedure is extremely simple with this technique, being similar to AAS with etv. The sample solution containing the ion to be determined is mixed with an added substance with which this ion forms stable diatomic molecules. Microvolumes (5 to 100 μℓ) of these solutions are introduced into the graphite tube cuvette. If a precipitate forms upon addition of the additive — through possible reaction with the analyte as well as with the matrix — separate reagent addition may be made directly into the graphite tube cuvette. The additive is first dosed, followed by the analyte-containing sample solution. Between these two dosages a drying step may be carried out. After dosage, the normal controlled program of electrothermal heating ensues: (1) dry phase, (2) ash phase, and (3) atomize phase (or preferably, an evaporation phase, in this case). For our studies, a Beckman-type 1268 graphite tube cuvette (U.S.) was used. The spectrochemical studies must be carried out using an appropriate AA spectrometer. A hydrogen hollow cathode lamp or a deuterium continuum light source is used. Both light sources have sufficiently similar UV intensity. A double-channel spectrometer should preferably be used as such a device permits background compensation even with MAS (according to the two-line method). For our studies, a type 811 Jarrell-Ash two-channel-two-beam spectrometer (U.S.) was used. Recording of the spectra is somewhat time consuming as they may only be obtained by point-by-point measurements at appropriate wavelengths.

Due to the great affinity to the halides for the metallic components, the stabilities of the respective diatomic molecules are rather high so that it was to be expected that results for the determination of halides would be as good as those obtained by MES.

We shall first describe the studies of the Japanese researchers. Yoshimura et al.[400] suggested the Cl^- be determined by InCl-MA at 267.2 nm. The SLA 100 carbon tube atomizer, and AA-1-Mark II spectrometer (Jarrel-Ash, U.S.), and a D_2 lamp light source were used. The spectrum was measured point-by-point between 264 and 269 nm ($\Delta\lambda = 0.1$ nm). Peaks were obtained at 267.2, 266.1, and 268.4 nm (compare with Reference 408). Using a sample of 5 $\mu\ell$, absolute detection limits of 8.7 ng Cl^-, 1.75 $\mu g/m\ell$ were obtained. Indium concentrations of 230 ng/5 $\mu\ell$ were used. Curvature of the calibration curves was observed. In a second paper,[401] the determination of F^- by AlF-MA at 227.5 nm was described. In this case, the dosage of the Al^{3+} was carried out first (as nitrate) followed by addition of the sample solution. Additions of Sr^{2+} and Ni^{2+} increased the signal and lowered the background. Field applications included the determination of F^- in biological samples and of F bound in organic compounds. Background compensation was carried out at 228.1 nm. The dependence of the signals from the spectral band width, ashing and vaporizing temperature, Al^{3+} concentration, and the concentration of other acids and cations was studied. As the half-width of the AlF-MA band is very narrow, operation is recommended at a spectral band width of 0.08 nm. Using 2.7 μg Al^{3+}, 0.021 ng $F^-/5\ \mu\ell$ could be detected. Explanation of the effect of the additives was not given.

Another paper[402] dealt with the determination of Cl^- and Br^- by AlCl- and AlBr-MA, respectively. An AA-8500 two-channel AA spectrometer and the FLA 10 graphite tube cuvette (Nippon-Jarrel, Japan) were used. The spectral band width was 0.16 nm. The following peaks were found: AlCl-MA, 261.4 nm, and AlBr-MA, 279.0 nm. Background correction was carried out at 260.1 and 281.5 nm. Additions of Sr^{2+} and Co^{2+} improved the signal-to-background ratio. No explanation for these effects was given. Using 2.7 μg Al^{3+}, 0.12 ng Cl^- and 1.2 ng $Br^-/5\ \mu\ell$ could be detected. Recently, the technique developed for F^- determination was modified .[403] Instead of the continuum light source, a Pt hollow cathode lamp was used. The line emitted from this lamp at 227.45 nm was used for measurement of AlF-MA. However, the background compensation was carried out with a D_2 lamp, as the Pt-I line at 226.88 nm is coincident with the Al-I line at 226.9 nm. As compared with the former technique, the detection limit changes by a factor of 0.5, i.e., 0.042 ng F^- could be detected, but the light intensity and reproductivity of wavelength adjustment as well as the reproducibility of the method are better.

The determination of fluoride in urine and blood serum was carried out by AlF-MA and with a fluoride-sensitive electrode.[404] The results were compared. For pure solutions, it was estimated that the values are accurate. The determination of F^- in blood serum showed that AlF-MA measurement gave values about 2 to 10 times larger than those obtained by ion-selective electrodes. These results suggest the existence of some protein-bound fluorine in blood serum.

Tsunoda et al.[405] describe the application of MAS of alkaline earth monohalides formed in a graphite tube to determine halogens. Molecular absorption bands of SrF and CaCl provided the highest sensitivities for the determination of fluorine and chlorine, respectively. The sensitivities of the MA of MgCl, CaCl, and SrCl are almost the same as those of AlCl, GaCl, or InCl. They concluded that MAS of the alkaline earths monochlorides has about the same analytical potentialities as those of AlCl, GaCl, and InCl. Takatsu et al.[406] determined fluorine in milk by AlF-MA. The content of 0.033 μg $F^-/m\ell$ milk was found for commercial bovine milk. It was shown there are many influences by many cations (compare with Reference 407).

A survey about occurrence of atoms and molecules of Al, Ga, In, and their monohalides in electrothermal furnaces was given by Tsunoda et al.[407] In the spectra some characteristic band structures have been identified for each metal halide.

Our studies began with a thorough investigation of the MA spectra of GaX and InX molecules (X = F, Cl, Br, and I) as well as GaO and InO molecules.[408] Spectra were measured between 190 and 400 nm. For the O-containing molecules, peaks were found at 240 nm (GaO) and 206 and 270 nm (InO), respectively. These bands, however, are very wide and probably represent dissociation continuum. For the X-containing molecules, the following maxima were found: GaF-MA, 211.4 nm; GaCl-MA, 248.2 nm (compare with Reference 409); GaBr-MA, 265 nm (wide band); InF-MA, 233.9 nm; InCl-MA, 267.2 nm; InBr-MA, 284.5 nm. GaI- and INI-MA could not be detected. It is striking that the A and B bands observed in emission hardly occur in absorption. The bands found are, in any case, the C bands (compare with Reference 52). Then we tried to develop some analytical methods.

There are some requirements for application of an analytical method in trace analysis. The most important requirement is the detection of the species to be measured. The detection limit depends on the sensitivity of the species and the reproducibility of the measurement. In our case, the detection limit depends on the absorption coefficient of the molecule in the gaseous state, the associated background absorption and its fluctuations, and the concentration of the molecules in the gaseous state. The absorption coefficient is related to the transition probability between the energy levels of the molecules. For a given molecule and transition, the absorption coefficient has a constant value. The concentration of stable molecules in the gaseous state dependes primarily on the dissociation energy of the molecules, the matrix of the sample, and the heating program of the graphite tube. These same factors also affect background absorption and the type of corrective action to be taken.

Another general consideration for using an analytical method in trace analysis is accuracy. The accuracy of our MAS determination is affected by the spectral influences on the background. These can be corrected or reduced by different methods of background compensation. First of all it is necessary to use effective methods for reducing matrix effects. This is possible by special optimization of the heating program. With an optimal heating program it is possible in some cases to separate traces from the matrix. Reduction of the matrix effects is also possible by modifying or adjusting the concentrations of certain constituents. In connection with this requirement we proved some molecular absorption systematically.

The alkali halides comply with some of the requirements of the methods since they form thermally stable salts; the basicity of the cations is very high, they are easily volatilized, they evaporate without decomposition, and their molecules have high dissociation energies. Therefore an attempt was made to observe absorption spectra of alkali halides, especially fluorides and chlorides. Absorption bands observed between 200 and 400 nm have low intensities, and therefore it is impossible to use these bands for analytical purposes. The most intense bands are given in Table 8. For each anion, the bands lie in the same wavelength region. The diatomic MX species of the alkaline earths have dissociation energies between 4 and 6 eV (compare with Table 9). We found sufficiently intense UV bands only for MgF and MgCl.[4-10] This was unexpected because their dissociation energies are the lowest of the alkaline earth halides. Three interpretations are possible.

1. The absorption coefficients of these species are very high.
2. Because Mg is easily volatilized, a low vaporization temperature is found.
3. The concentration of MgX in the vapor phase is higher than that of the other alkaline earths which form more stable MO species.

Table 8
DISSOCIATION ENERGIES (E_D), BOILING POINTS (B_p), AND WAVELENGTHS (λ) OF ABSORPTION BANDS IN THE UV FOR SEVERAL ALKALI HALIDES[50-53,458]

	E_D(eV)		B_p(°C)		λ(nm)	
Metal	F	Cl	F	Cl	F	Cl
Li	6.0	4.8	1254	1350	—	226.7
Na	5.0	4.2	1700	1440	211.8	237
K	5.2	4.4	1500	1411	214	246
Rb	5.1	4.6	1410	1385	211.5	247
Cs	5.3	4.5	1251	1300	—	245

Table 9
DISSOCIATION ENERGIES (E_D) OF 1:1 SPECIES (MX), BOILING POINTS (B_p) OF 1:2 SPECIES (MX_2), AND WAVELENGTHS (λ) OF ABSORPTION BANDS OF ALKALINE EARTH HALIDES IN THE UV[50-53,458]

	E_D(eV)		B_p(°C)		λ(nm)	
Metal	F	Cl	F	Cl	F	Cl
Be	6.0	4.0	—	520	301.8	—
Mg	4.8	3.3	1260	1418	358.2 268.3	376.2
Ca	5.5	4.1	1500	1940	330	—
Sr	5.6	4.2	2489	1250	—	—
Ba	6.1	4.6	2250	1556	—	—

We investigated the influence of several matrices on the intensity of the MgF- and MgCl-MA and found that the influence of Na^+, Sr^{2+}, and Cu^{2+} on the signals depends on the nature of the ion and is very different. Sodium and strontium ions depress the MgX-MA because they react in the vapor phase. The degree of the reaction depends on the relation between the dissociation energies and the evaporation temperatures.

There are influences of Cu ions on MgF- and MgCl-MA. In the case of MgCl, the signal is increased by Cu ions. We investigated this observation and found the following explanation. MgCl forms the oxide by hydrolysis during the drying and ashing step in the graphite tube. In the presence of Cu^{2+} ions in the solution, a complex between the Cu^{2+} and Cl^- ions is formed. In the drying and ashing step, this complex forms a thermally stable CuCl. After evaporation of CuCl and Mg or MgO, MgCl is formed in the vapor phase. The chloride concentration can be determined at 376.2 nm in the absence or presence of Cu^{2+} ions with the reciprocal sensitivity for 0.01 A of 9.7 and 5.8 ng of Cl^-, respectively. In the case of MgF, there is practically no influence from Cu since the MgF_2 molecule is an insoluble, stable salt for which high temperature hydrolysis is much smaller. The analytical results show that it is possible to determine 2.4 ng of F at 358.2 nm and 5.7 ng of F at 268.3 nm in the presence of 10 μg of Mg^{2+} in 10 $\mu\ell$.

The spectra of the halides of the Al, Ga, In, Tl group were investigated by us in detail.[408,409,411-414] The dissociation energies and the wavelength of the most intense absorption bands of these molecules are shown in Table 10. It is surprising that only the TlI molecule, which had the smallest dissociation energy, provided absorption bands of iodine.[414] The reason for this result is the formation of the insoluble and

Table 10

DISSOCIATION ENERGIES (E_D) AND ABSORPTION BANDS OF MX SPECIES OF THE HALIDES OF THE THIRD GROUP METALS IN THE UV[51-53,458]

	E_D(eV)				λ (nm)			
Metal	F	Cl	Br	I	F	Cl	Br	I
Al	6.8	5.1	4.1	—	227.5	261.4	279.0	—
Ga	6.0	4.9	4.2	3.5	211.4	248.2	268	—
In	5.5	4.5	4.2	3.4	233.9	267.2	284.5	318
Tl	4.4	3.8	3.4	2.9	244	251.9	266.8	202

thermally stable TlI in the graphite cuvette. This salt evaporates with the other Tl salts since all Tl salts are very volatile. This means that the concentration of Tl atoms is very high in the vapor phase and the equilibrium Tl + I ⇌ TlI is shifted in the direction of TlI.

Some practical results of the optimization of the conditions for analytical determinations in relation to our given supposition are now presented. The MA depends on the metal concentration. Because the AlX molecules have the highest dissociation energy, the necessary excess concentration of metal is not as high as in the case of the less stable MX molecules. The optimum for Al was found at 1 to 2 $\mu g/10\ \mu l$. For the other metals, this value lies at 10 to 20 $\mu g/10\ \mu l$.

Addition of Na^+ ions influences the absorption intensity of AlX-MA significantly; the influence on other MX-MA was not as strong. In the case of Al halides, we have observed a strong thermal hydrolysis during the drying and ashing step which is depressed by addition of Na^+. In the case of In halides, the influence of Na^+ is smaller because In is the strong basic element. Nevertheless, in the presence of high Na^+ concentration, the InF-MA is depressed because the dissociation energies of NaF and InF are simliar and the equilibrium between NaF and InF molecules is shifted in the direction of higher concentration of NaF.

The AlF- and AlCl-MA is influenced by the addition of some bases.[409] The signal increased because thermal hydrolysis was depressed. The greatest increase was found by addition of $Sr(OH)_2$ and $Ba(OH)_2$. This effect is caused by a reduction of the volatilization of Cl^- and F^- ions by the Sr^{2+} and Ba^{2+} ions. Therefore Cl evaporates later and the maximum concentration in the upper phase of Cl^- and F^- and the less volatile Al occurs in time.

The analytical results show that it is possible in any case, but especially for F^- and Cl^-, to determine these elements at nanogram levels[409] (compare with Table 11). Such determination is influenced by the presence of other halides. Chloride ions produce the strongest influence for F^- determinations because they form stable molecules with the metals. In the presence of a large excess of Cl^- ions, the equilibrium between MF and MCl is shifted in the direction of MCl.

The strong influence of F^- ions on the AlCl- and GaCl-MA is obvious because fluoride forms a more stable molecule than does chloride. Also, the influence of bromide and iodide was significant. This can be related to the relative stablility of the MCl molecules and the stabilities of MBr and MI. No influence of F^- ions on InCl-MA was observed. On the surface, this result is surprising because the dissociation energy of InF is higher than that of InCl. In this case, there is an effect of evaporation. Because In^{3+} ions are strong bases and HCl is a strong acid, it is not necessary to add Na^+ ions for the stabilizatiion and for the depression of thermal hydrolysis. Since HF is only a weak acid, the InF × n H_2O residue is decomposed in the ashing step by thermal hydrolysis. This means that we have a separation of trace metals and matrices. The con-

Table 11
ANALYTICAL RESULTS OF THE DETERMINATION OF X$^-$ TRACES BY MOLECULAR ABSORPTION OF AlX, GaX, InX, AND MgX

	Reciprocal sensitivity in ng/0.01 A			
Metal	F$^-$	Cl$^-$	Br$^-$	I$^-$
Al	0.4	1.6	18	—
Ga	0.8	9.0	—	—
In	1.1	3.0	130	—
Tl	—	—	50	80
Mg	2.4	5.8	—	—

Table 12
ANALYTICAL CHARACTERISTICS OF THE DETERMINATION OF HALOGEN TRACES IN THE PRESENCE OF THE OTHER HALOGENS

	Absolute reciprocal sensitivity	Permissible excess of other halogens			
Species	(ng/0.01 A)	F	Cl	Br	I
AlF	0.4	—	$5 \cdot 10^4$	10^5	10^5
GaF	0.8	—	$5 \cdot 10^3$	10^4	$5 \cdot 10^4$
InF	1.1	—	10^4	10^4	$5 \cdot 10^4$
MgF	2.4	—	$2 \cdot 10^4$	$4 \cdot 10^4$	$4 \cdot 10^4$
AlCl	1.6	10^4	—	10^3	10^3
GaCl	9.0	10^2	—	$5 \cdot 10^2$	$5 \cdot 10^3$
InCl	3.0	10^5	—	10^3	10^3
MgCl	5.8	10^3	—	$5 \cdot 10^2$	10^2
AlBr	18	10^2	$5 \cdot 10^2$	—	10^3
InBr	130	10^2	10	—	10
TlBr	50	$5 \cdot 10^2$	10	—	10^2
TlI	80	$5 \cdot 10^2$	10^2	10	—

centration ratios for the determination of halogens in the presence of other halogens are shown in Table 12. It is shown that it is possible to determine traces of halides, especially of F$^-$ and Cl$^-$, in the presence of other halides up to an excess of 10^5.

Only a few investigations were carried out with heavy metals.[398, 399] The main point of this investigation was the evidence of the depressing influences of the Cl ions on the AAS of Zn, Cd, Mn, Pb, Cu, etc. The formation of appropriate molecules was found only for copper. Direct MA was also found in the case of AgCl, AgBr, and AgI molecules.

In Table 13, the dissociation energies are very low. However, because these elements form insoluble, thermally stable, easily volatile salts, it is possible to determine these molecules in the graphite cuvette at lower temperatures. Nevertheless, their analytical application for the determination of chloride is less useful.[67,68]

It is known that the Ge-AA is depressed by sulfuric acid. We sought the reason for this signal depression. The spectrum of appropriate mixtures shows intense absorption bands as 215.2, 288.8, 285.1, and 292.1 nm. The bands at 290 nm are known as the D

Table 13
DISSOCIATION ENERGIES, MOLECULAR ABSORPTION BANDS, AND ANALYTICAL RESULTS FOR SEVERAL HEAVY METAL HALIDES

Molecule	E_D(eV)	Wavelength (nm)	Reciprocal sensitivities (ng/0.01 A)
CuCl	3.6	221.5	200
AgCl	3.2	314	250
AgBr	3.2	318.4	150
AgI	2.6	320.1	180

system of GeS. The first band at 215.2 nm has not been previously reported. We explained theoretically and experimentally what species caused this band (compare with Reference 415). The dissociation energy of GeS is very high (5.7 eV). However, the dissociation energy of GeO, which can also be formed in the vapor phase, is higher (6.8 eV). In principle it is also possible that GeO molecules caused this band, but by variation of the compositions of solutions and atmospheres, e.g., in SO_2 atmosphere, it was shown that the band at 215.2 nm is also caused by S-containing species. In the absence of Ge, it was established that under special thermal conditions there is a wide SO-MA band only at 240 nm. The dissociation energy of this molecule is 5.3 eV. This means that SO_2 is destroyed and SO_2 and SO molecules do not cause the band at 215.2 nm. Therefore, we could conclude that only species containing Ge and S cause the band at 215.2 nm. A second reason for this conclusion is that the influence of several matrices on the intensity of the MS is the same for the bands at 288.8 and 215.2 nm. This means that the GeS molecule caused this band.

GeS-MA was found in the presence of Na_2S, Na_2SO_4, H_2SO_4, Na_2SO_3, and NaSCN and of the optimal amount of Ge (7.5 $\mu g/10\ \mu l$). The thermal conditions depended on the composition of the solution, e.g., acidity. In some cases, the acidity can lead to the volatilization of the sulfur compounds. In the simplest case, Ge^{4+} and H_2SO_4, there is a thermal hydrolysis which can be depressed by the addition of Na^+ ions. By using the influence of the pH of the solution on the evaporation, it is possible to determine S^{2-} and SO_4^{2-} in the same solutions. At pH 5, H_2S is volatile in the ashing step and only SO_4^{2-} ions are determined. At pH values higher than 10, it is possible to determine SO_4^{2-} and S^{2-} ions. The reciprocal sensitivity is 50 ng S per 0.01 absorbance for optimal thermal conditions.

In the course of our investigations, we found some generally applicable principles which should be used for the optimization of analytical methods based on MA in the graphite tube. These points of view will be treated in the order of the processes occurring in each MAS procedure. They show how it is possible to get higher molecular concentration in the vapor phase to fulfill the main requirement.

a. *Aliquotting and Drying*

Preparation of solutions is possible either by previous mixing of the sample and the additional solution or by mixing them directly in the graphite cuvette. This first procedure is very important because it influences not only the drying step but also each of the following processes in the graphite cuvette. Most important is to avoid volatilization of the easily volatile, usually anionic, nonmetallic components during the drying phase. This can be done by forming thermally stable salts. There are several possibilities.

1. High pH values by addition of alkali hydroxide — however, the presence of an excess of alkali metal atoms leads to a decrease of the MA signal. This is due to the reactions in the vapor phases; the alkali metal atoms react with molecules to form alkali metal molecules

$$M_lX + M_{alk} \rightarrow M_l + M_{alk}X \qquad (12)$$

2. Addition of an excess of the M compound — in this case, all anions will be bound. Also in this case it is possible that a large excess will result in signal depressions. This is caused by its high boiling point or by carbide formation, e.g., in the case of Al.
3. Addition of an additional M compound, which forms an insoluble salt with the determined anion — such stabilization is possible only when the solutions are added subsequently into the graphite cuvette. Very good results were observed when the insoluble salt is directly evaporated forming the molecule, e.g., TlI, AgCl, etc. In this first step, the heating program is not so important.

b. Ashing

The most essential problem of the ashing step is the thermal separation of traces and matrix. In the case of AAS, it is realized by an appropriate heating program. In AAS it is necessary to avoid the volatilization of the element to be determined. In the case of MAS, it is necessary to avoid the volatilization of both components which may form the molecule. This is difficult especially for the anionic component because these components are very volatile in most cases. A special problem is the high temperature hydrolysis of the dry solid residue which contains crystalline water. The hydrolysis proceeds according to the equation:

$$MX_n^x mH_2O \xrightarrow{\text{h. temp.}} MX_{n-1}OH \times mH_2O + HX\nearrow \qquad (13)$$

In all cases, when we take a salt of a weakly basic metal, e.g., Al or Ga, which contains water, at elevated temperatures a reaction occurs giving rise to oxides with volatilization of the anionic component. Addition of strongly basic compounds, e.g., alkali or alkaline earth metals, makes it possible to avoid volatilization. Another possibility consists of the appropriate choice of a lower ashing temperature.

c. Evaporation and Formation of Molecules:

In this process, molecules which have high absorption coefficients ought to be evaporated or generated in the vapor phase. The yield of the molecules in relation to the amount of halide in the analyte solution should be very high. It is necessary that all these molecules, as in AAS where atoms are generated, are simultaneously present in the plasma. Only by the fulfillment of these conditions can a high absorption signal be found. This occurs when stable molecules are considered and simultaneous evaporation of the M and X component takes place. The first assumption is accomplished if diatomic molecules have dissociation energies between 4 and 6 eV.

In favorable cases at low plasma temperatures, the concentration of less stable molecules ($E_D < 4$ eV) is also high enough for measurements. This is valid for elements of the first three groups which combine with elements of the seventh main group.

A high yield of the molecules was obtained by influencing the equilibrium of dissociation of the molecules in the plasma by using an excess of the M compounds. The simultaneous evaporation of the M and X compounds is not easily realized because the X compounds are in most cases more volatile. A simple case occurs when a solid which is formed in the cuvette in the course of drying and ashing evaporates without decomposition.

This situation is observed for the alkali and alkaline earth metal halides and, in part, also for Ag and Tl halides. In other cases, quite volatile cations for the M compound were used. Finally, it is possible to reduce the volatilization of X^- ions by formation of appropriate molecules and salts. Such cases are also known in AAS, where the high volatility of Se compounds is reduced by the addition of Ni(II), which forms stable NiSe. In the MAS case, the alkaline earth metals effectively reduce the volatilization. These elements have sufficient basicity, are not very volatile, and form stable compounds with their free valances with the carbon of the graphite tube. It was concluded that there are many problems which have to be optimized for a good analytical result. In comparison to AAS, MAS has more serious problems because of the stronger matrix effects.

In conclusion, it is possible to determine traces of halides and also sulfur in microsamples using spectra of their diatomic species. Because there exist many interferences by matrix substances, it is best to separate the traces from the matrix substances by extraction, precipitation, or distillation methods.

For Br^- and Cl^- determinations, we developed an extraction-MAS method.[416-417] We extracted the halides with triphenyltinhydroxide in *o*-xylene. The halide is then back extracted with a 0.025 *M* solution of $Ba(OH)_2$ in water and then a microvolume of Al^{3+} solution is added. The AlCl-MA and AlBr-MA are measured at 261.4 nm and 279.1 nm, respectively. By preconcentration and separation it is possible to determine Cl^- concentrations of 8×10^{-7} mol/*l* and Br^- concentrations of 6×10^{-6} mol/*l*. Relative to some solid inorganic nitrates, it is possible to determine 0.5 ppm chloride and 10 ppm bromide. This is an improvement of 1000-fold in comparison to the determination without extraction.

Similar work was done for the improvement of F^- determinations. Fluoride was extracted by triphenylantimonydihydroxide in MIBK and back extracted also with 0.025 mol/*l* $Ba(OH)_2$ containing the appropriate amount of Al^{3-} ions.

For photographic applications it is necessary to determine the relation between AgCl and AgBr. The MAS of AlCl was used for the determination of Cl in the mixture after the addition of Al^{3+} [419] and dissolving a part of the sample in NH_3. NH_3 concentration must be optimized because it is necessary to solve all AgCl but only a small amount of the AgBr. By using 2 to 4 mg of the AgCl and AgBr mixture it is possible to determine down to a minimum concentration of 0.5% AgCl with a precision and accuracy of about 5%.

In the determination of Cl in Cl-doped semiconductor Se, this element is a great problem because there are many disturbances by Se compounds for any Cl determinations. Besides this, sometimes bromine is found in the Se semiconductor. Then the specific determination of Cl in Cl-doped Se is practically impossible by polarographic methods. Therefore, we developed a method using AlCl-MA. After dissolving the doped Se in $AgNO_3/HNO_3$, the AgCl formed coprecipitated with Al_2O_3. From this precipitate, the AgCl is dissolved by ammonia. After addition of $Ba(OH)_2/Al^{3+}$ solution, the AlCl-MA at 261.4 nm is measured. The detection limit relative to 500 ng of Se is 0.2 ppm Cl. The method is specific for Cl. In a similar manner it is possible to determine Br. For the Cl-determination, a tenfold excess of Br does not affect it (compared with Reference 420). In the epitaxial procedures for the formation of some $A^{III}B^{V}$ semiconductor materials, MCl_3 is often used. Therefore it is possible that small amounts of Cl are present in the $A^{III}B^{V}$ crystals. For determination of these Cl traces, we dissolved the materials in HNO_3 and distilled the formed HCL into a $AgNO_3/HNO_3$ solution. After this, the determination procedure is the same as for Se (compare with Reference 420); 0.2 ppm Cl can be determined in 500 mg of an appropriate semiconductor.

In Table 14 a survey about trace determinations using MAS in electrothermally heated graphite tube cuvettes is given.

Table 14
ANALYTICAL APPLICATIONS OF MOLECULAR ABSORPTION IN CARBON FURNACE ATOMIZERS

Molecule	Dissociation energy (eV)	Band (max.) nm	Ion determined	Detection limit	Substance	Ref.
AlF	6.8	227.5	F^-	0.02 ng		401
				0.03 μg/m*l*	Milk, blood	404, 40
	6.8	227.5	F^-	0.04 ng	—	412
	6.8	227.5	F^-	10^{-7} *M/l*	Extraction	418
GaF	6.0	211.4	F^-	0.8 ng	—	411, 41
InF	5.3	233.9	F^-	1.1 ng	—	412
MgF	4.75	358.2	F^-	2/1.5 ng	—	405, 41
	4.75	268.2	F^-	8 ng	—	410
CaF	5.5	606.4	F^-	0.5 ng	—	399
SrF	5.6	662.9	F^-	0.4 ng	—	405
BaF	6.05	500.5	F^-	1.5 ng	—	405
AlCl	5.1	261.4	Cl^-	0.12 ng	—	402
	5.1	261.4	Cl^-	1.6 ng	—	409
	5.1	261.4	Cl^-	10^{-7} *M/l*	Extraction	416
	5.1	261.4	Cl^-/Cl	0.2 ppm	500 mg Se	420
	5.1	261.4	Cl^-	0.2 ppm	$A'''B^{V}$ comp.	420
	5.1	261.4	Cl^-, AgCl	0.5%	AgBr	419
GaCl	4.9	248.2	Cl^-	9 ng	—	409
InCl	4.5	267.2	Cl^-	8.7 ng	—	400
	4.5	267.2	Cl^-	3 ng	—	409
MgCl	3.2	376.2	Cl^-	50 ng	—	410
	3.2	269.3	—	—	—	410
CaCl	4.2	621.2	Cl^-	0.6	—	405
SrCl	4.2	461.1	Cl^-	2.0	—	405
BaCl	4.6	514.1	Cl^-	2.4 ng	—	405
AlBr	4.6	279.0	Br^-	1.2 ng	—	402
	4.6	279.0	Br^-	10^{-6} *M/l*	Extraction	416
InBr	4.2	284.5	Br^-	130 ng	—	413
TlBr	3.4	266.8	Br^-	140 ng	—	413
	3.4	343.2	Br^-	50 ng	—	413
TlI	2.9	202.0	I^-	80 ng	—	414
	2.9	380.4	I^-	160 ng	—	414
GeS	5.7	215.2	S^{2-}, SO_4^{2-}, SCN^-, SO_3^{2-}	50 ng S	—	415

VI. MOLECULAR FLUORESCENCE SPECTROMETRY (MFS) OF DIATOMIC MOLECULES

As was the case with the late development of atomic fluorescence spectrometry (AFS) as compared with AES and AAS, MFS was developed mainly in the course of the last few years.

Apart from merely physical studies of the spectroscopy of selected species, there are only a few publications with analytical purposes in the field, such that particular structuring of this section is not necessary. The reasons for this state of the art are mainly due to the expensive light sources, their somewhat unfavorable criteria of application, and problems in the relation between intensity and concentration and the ensuing poor sensitivity obtained.

There is a very large survey about laser-induced MF in flame chemistry (see Reference 421). In this publication, many scientists gave information about the state of the art. Daily[422] examined the nature of laser-induced molecular fluorescence in detail and discussed all theoretical aspects (31 references are given). Bechtel[423] explains that temperature measurements are possible in flames by using laser excitation (18 references were given). Müller et al.[424] showed that low-power laser fluorescence measurements of OH, S_2, SH, SO, and SO_2 are possible (20 references were given). Cottereau et al.,[425] Kotlar et al.,[426] and Lucht et al.[427] studied the laser-induced fluorescence of the OH radical in flames.

The paper of Grieser and Barnes[428] has a more analytical purpose. They showed that it is possible to detect NO molecules in atmospheric pressure flames. Detection sensitivity in the parts per million was observed with laser pulse energies in the range of about 3 μJ.

Besides this general information there are some original papers. Barnes et al.[429] applied a dye laser to the study of MFS in flames. Through excitation at 431.2 nm, the 0.0 band of the Q branch of the CH radical could be observed at 431.5 nm.

These studies were not applied for analysis. Somewhat later, Human and Zeegers[430] studied MX-containing molecules such as CaOH, SrOH, and BaCl. They excited MF with a continuum light source. The molecules were generated in an $Ar\text{-}H_2\text{-}O_2$ flame. They found that after absorption of radiation redistribution of the energy took place such that there was no dependence of the wavelength of the fluorescence light on the energy distribution of the exciting radiation. The fluorescence yields in MFS are reported to be of the same order of magnitude as in AFS.

Winefordner et al.[431] reported on the determination of PO_4^{3-} by PO-MF. PO_4^{3-} is introduced into an Ar-separated H_2 air flame and excitation of MF is obtained using a Xe arc lamp; 80 μg PO_4^{3-} may be detected. These studies were extended to the determination of the MF of other species which normally occur as background over-laying AFS in flames.[432] The following data were given: (1) PO-MF occurs between 323 and 330 nm (transition $B^2\Sigma - X^2\Pi$) and between 220 and 275 nm (transition of the γ system); (2) NH-MF at 326 nm; (3) CN-MF at 388.3 nm; and (4) OH-MF between 305 and 320 nm and also between 280 and 295 nm.

In another paper,[433] laser-excited MF of CaOH and SrOH molecules was described. These molecules were generated in a C_2H_2 air flame and excited with a pulsed N_2-pumped tunable dye laser with sufficient excitation; the following MF bands were observed: CaOH: 533.9 nm, between 622 and 623 nm, and at 603 nm; SrOH: 606 and 682 nm. The studies served, above all, for elucidation of the energy-level diagram of the CaOH system.

MF of CrO and MnO molecules is also reported.[434] The same authors succeeded in detecting MF of BaO, BaOH, and BaCl molecules;[435] in this paper, some information on the present level of the technique is given. It is pointed out that MF was also observed with CaX, SrX, BaX (X = F, Cl, Br, I),[436,437] with AlO and BeO[438,439] in NaH[440,441] and with CdH molecules.[442] With Ba species the following bands were found: BaOH- and BaO-MF: 512, 496.5, and 487 nm; BaO-MF: 535 nm; BaCl-MF: 506.6, 513.6, 516.7, 521.3, 524.1, and 532.1 nm.

MF was also observed for the fluorides of heavy metals such as GeF,[443] SnF,[444] and PbF.[445] However, hardly any of these studies were used for analytical purposes. By CH-MF at 431.5 nm and CN-MF at 388.3 nm, Bonczyk and Shirley[446] recently determined the concentration of these molecules in C_2H_2 air and $C_2H_2\text{-}N_2O$ flames (60 and 150 ppm, respectively) using laser-excited saturated fluoresence.

More recently DeVlieger at al.[447] described the fluorescence of Br_2 molecule excited by a single-mode krypton-ion laser. In a similar manner, the fluorescence of I_2 molecules was described.[448] Some papers give information about temperature determination in flames.[449] Bechtel[449] determined temperatures of the OH radical and of molecular nitrogen in premixed laminar flames by laser technique. Chan and Daily[450] used the laser-induced fluorescence of the OH radical for measuring translational flame temperature. Zizak et al.[451] determined the flame temperature by measuring of the OH (0.0) fluoresence at 308.154 nm. The ICP as a source for MF was studied by Tallant.[452]

The NH-MF excited by CO_2 laser was measured by Hawazaki et al.[453] at 336 nm. Wijchers et al.[454] used a continuous wave (cw) dye laser-induced fluorescence for the excitation of the YO molecule. Koizumi et al.[455] used the Zn-resonance line at 213.8 nm for excitation of the SO_2 fluorescence. They shifted the line by magnetic field to get a maximum fluorescence intensity. The lower detection limit was 5 ppm SO_2.

From this starting point, the tunable atoms line molecular spectrometry (TALMS) method was developed.[456] The method is highly specific and depends on the Zeeman effect to tune an atomic emission line to coincide with a sharp molecular absorption feature. It has determined NO, NO_2, SO_2, and H_2CO.

Donnelly and Krlicek[457] developed laser spectroscopic methods for the detection of PH_3, P_2, AsH_3, As_2, InCl, and GaCl using both tunable dye laser-induced fluorescence and excimer laser excitation. No detection limits are reported.

VII. CONCLUSIONS

With regard to the analytical performance of molecular spectrometry of diatomic molecules, and according to the comments made in the first section concerning analytical criteria and performance data, the following assessments may be made.

Molecular spectrometry of diatomic molecules has provided great impetus to the elucidation of the matrix effects, particularly in AS procedures. In this connection it does not matter whether measurements of the molecular spectra are made in emission or in absorption; what is significant is in the detection of the molecules themselves. It was shown that molecules formed from the matrix, both with AAS and AES techniques, may greatly affect the background observed in MA or ME techniques. Factors influencing signals, above all, signal depressions with AAS, were also elucidated by MA studies. The most important results are (1) in electrothermally generated vapors in graphite tube cuvettes, both signal depressions and background absorptions play a more important role than in flames (this is due to the thermal heterogeneity of the vapor in the graphite tube); and (2) molecules are formed predominantly from the M components on the one hand and from the X (X = F, Cl, Br, I, O, S) components on the other hand. With every analysis using techniques of atomic spectroscopy in low temperature vapors, the analyst must check whether or not such factors which may alter the accuracy of the results are present. Adequate methods for correction may then be deduced.

The second merit of molecular spectrometry of diatomic molecules arises from the fact that it is a useful tool for the quantitative analysis of nonmetallic elements in the field of trace analysis. Applying the analytical criteria mentioned in the first section for judging this merit, the following evaluations may be given.

The limit of detection — characterized by sensitivity and reproducibility — is good; flame techniques provide better reproducibility than cuvette techniques; the sensitivity is, however, greater with cuvette techniques. Consequently, the limit of detection, calculated by the 3-sec criterion, may be assessed as being better with cuvette techniques in most cases. This result agrees in general with trends in AS. However, conditions are not so obvious in the field of molecular spectrometry wherein chemiluminescent athermal excitation in flames produces favorable conditions for emission.

Accuracy — characterized by spectral selectivity and matrix effects — is a difficult problem similar to that encountered in MES and MAS. The spectral selectivity of spectrometers is generally excellent. As bands occur with MS (different from AS), there are frequent spectral overlaps. Overall, the spectral selectivity of the technique is, however, good. As compared with AS, the matrix effects play an even greater role. On the one hand, special compositions of solutions for the formation of the molecules, which are interesting for spectroscopy, are necessary; on the other hand, these complex chemical compositions had a direct influence on band intensity. In this context, a significant role is played by the thermal characteristics of the vapor. It realizes a very constant temperature interval because the optimal molecule concentration in the vapor is influenced by the evaporation and the dissociation. Because the temperature and also the composition of vapors of unknown samples is not constant, the standard addition technique is better for the analysis of unknown samples than the calibration curve technique. Another possibility to improve the accuracy of the measurements consists of combining the MA technique with separation (or preconcentration) methods. Then it is also possible to use the calibration curve technique. Even more than with AS procedures it must be realized that there is always a very small temperature interval within which vapor composition, and thus concentration of the analyte molecules, may be regarded as constant.

The applicability of the method is much more limited as compared with AS, for it is virtually restricted to the elements B, C, Si, N, P, As, Sb, O, S, Se, Te, F, Cl, Br, and I. It must be noted that, to date, mainly halogens, nitrogen, boron, and sulfur have been determined by ME and MA techniques.

Both in MES and MAS there are microtechniques permitting the analysis of microsamples. Simultaneous multielement analyses have not yet been developed. The linear concentration range generally spans one order of magnitude. Curvature of calibration curves is due to the molecule formation. Overall, these techniques, particularly for some of the elements mentioned, serve to compliment those of AS.

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